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# Contamination in glove materials and the effectiveness of cleanup methods with exposure to granular pesticides

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# Contamination in glove materials and the effectiveness of cleanup methods with exposure to granular pesticides

by

Chuanpu Guo

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## ABSTRACT

The purposes of this study were (1) to determine the effects of various exposure times and pesticide composition on contamination levels and breakthrough times of nitrile, neoprene, and barrier laminate glove materials exposed to two granular pesticides: terbufos (Counter® 20CR) and tefluthrin (Force® 3G) and (2) to determine the effects of cleanup methods, detergent, and laundering temperature on reduction of pesticide contamination.

Three experiments were conducted. In experiment 1, breakthrough time and contamination levels were studied by exposing alpha-cellulose backed glove material specimens to pesticide granules in petri dishes for set time periods up to 24 hours. In experiment 2, contaminated specimens were flushed with a flow of water or washed in a Launder-Ometer, using a set laundering protocol. In experiment 3, the 30-minute exposure was followed by Launder-Ometer washing at two temperatures with and without detergent. Pesticide residues in glove specimens and cellulose pads were extracted with solvent. Residues in water solution were extracted with solid phase extraction. Gas chromatographs were used for residue analysis. Factorial analysis of variance was used to determine statistical differences in the various experimental treatments. Linear regression was used to identify whether there was a linear relationship between contamination and exposure time.

The breakthrough time of glove materials to granular terbufos or tefluthrin was more than 24 hours. A positive linear relationship between contamination and exposure time was found. Pesticide composition, glove material, exposure time, cleanup methods, and detergent significantly affected the reduction of contamination. The data show that barrier laminate should be a single-use material, as it is advertised. Reuse of neoprene gloves cannot be recommended based on chemicals and cleanup methods investigated. Cleanup of neoprene was somewhat successful with low toxicity chemicals, depending on exposure time and cleanup method. Cleanup of granular contamination was most successful with nitrile gloves, with about 66% of terbufos and 90% of tefluthrin removed by flush or Launder-Ometer wash. Pesticide also was found in laundering water solutions. The amount of pesticide in water solution varied with pesticide type, glove material, exposure time, cleanup method, and laundering parameter.

# CHAPTER 1. INTRODUCTION

Today various types of pesticides are widely used across the world in agriculture, government, home, and garden. In 1995, user expenditures for pesticides in the United States totaled $11.3 billion, accounting for nearly one-third of the world market. Presently, in the U.S. about 21,000 pesticide products and 875 active ingredients are registered for marketing and use (Aspelin, 1997).

Pesticides currently are one of the important tools in modern agricultural production. Agriculture is the largest pesticide user, consuming more than two-thirds of the pesticides sold in the United States. Since the 1960s, annual pesticide usage in U.S. agriculture has increased from about 400 million pounds to an estimated 800 million pounds, currently worth $7.9 billion (Aspelin, 1997).

In agriculture in the United States of America, terbufos (Counter®) and tefluthrin (Force®) are widely used as insecticides for the control of soil pests in corn. In Iowa, Counter® ranked second and Force® ranked fourth on the list of insecticides used for corn in terms of total quantity applied. In 1995, Iowa farmers used about 1 million pounds of Counter® and 46,000 pounds of Force® on 11.7 million acres of corn. In the entire nation, the two pesticides were applied to 71.2 million acres of corn (Sands & Holden, 1996).

Pesticides, which are used to protect crops from insects, weeds, and disease, have made an important contribution toward the increased productivity of American farmers. One hundred years ago, each American farm worker supplied enough agricultural products for three people. By 1950 one farm worker produced enough for 14 people and by 1990 enough for 96 people. In American agricultural production, insects, weeds, plant diseases, and nematodes result in crop losses of approximate $30 billion every year (Ware, 1994). The effective use of pesticides makes it possible to save approximately an overall one-third of U.S. crop production (Bohmont, 1990).

The widespread use of pesticides, however, also creates environmental and health problems. There is a dilemma about pesticide use. On the one hand, modern agricultural production has a heavy dependence on pesticides to control pests, weeds, and plant diseases. On the other hand, pesticide usage has harmful effects on human health, environment, wildlife, nontarget plants, and insects. In recent decades, there have been increasing concerns about human pesticide exposure, especially among farm workers (Rucker et al., 1988).

Farm workers' exposure to pesticides is through three routes of entry into the body (Bohmont, 1990): oral exposure; inhalation, or respiratory, exposure; and dermal exposure. In agriculture, routes of oral exposure are accidental splashing of pesticides into the mouth or food handled with contaminated hands. The respiratory system may be exposed to pesticides by

inhalation of fine particles, powders, and vapors. Comparing oral exposure and respiratory exposure, pesticide absorption through the skin is the most important route of entry into the body (Moraski & Nielsen, 1985). Pesticide absorption through skin contact may be due to a splash, spill, or drift when mixing, loading, and applying pesticides. Exposure also can occur by contact with crop residues or when cleaning or repairing equipment contaminated by pesticides.

In most dermal exposure cases, the skin of the hands may have greater exposure than any other parts of the body (Keeble, Correll, & Ehrich, 1993). Wearing gloves is thought of as one effective and practical means to decrease pesticide exposure when farmers mix, load, and apply pesticides. In a study on the exposure of pesticide applicators to nitrofen, Putnam, Willis, Binning, and Boldt (1983) found that wearing gloves significantly decreased hand exposure to pesticides. Although chemical resistant gloves can prevent applicators from overexposure to pesticides, the effectiveness of chemical resistant gloves in the reduction of pesticide exposure was still unknown (Stone, Wintersteen, & Padgitt, 1994).

During the past two decades, studies have been conducted to evaluate resistance of chemical protective materials to permeation by pesticide using standard ASTM test procedures that were developed for measuring liquid permeation. The research has focused on the permeation resistance of chemical protective materials to liquid pesticides (Ehntholt et al., 1990; Jencen &

Hardy, 1988, 1989; Moody & Ritter, 1990). Other research (Braaten, 1988; Stone et al., 1992a) investigated the contamination of cotton fabrics by granular pesticide. A study on the contamination of chemical resistant gloves by granular pesticides and subsequent cleanup has been conducted by Stone et al. (1995). Studies on the permeation resistance of chemical protective materials by granular pesticides were not considered high priority because granular products were viewed as much safer for use than liquids. However, many granular pesticides, especially granular insecticides, remain highly toxic and have a danger label. When farm workers handle granular pesticides, pesticides can enter the worker's body through contact with the skin of the hands. The lack of studies on the permeation resistance of chemical protective materials by granular pesticides might be attributed to the lack of a standard test method for such a study. Measurement of permeation resistance of chemical protective materials by granular pesticides is difficult and complicated.

It is recommended by experts and educators of Extension service that after protective clothing is used, it should be cleaned and decontaminated through laundering to reduce the pesticide residue in clothing (United States Environmental Protection Agency, 1993; Stone, Higby, & Stahr, 1992b). Several researchers (Kim, Kadolph, & Stone, 1988; Laughlin & Gold, 1990; Laughlin, Newburn, & Gold, 1991; Raheel, 1987; Stone et al., 1993) have investigated the effectiveness of laundering

procedures for decreasing pesticide contamination in work clothing fabrics. Laughlin and Gold (1988) stated that effectiveness of laundering was related to the type and formulation of pesticides, the pattern and time of pesticide exposure, and laundering factors such as water temperature and detergent.

However, almost all research on the effectiveness of laundering for decreasing pesticide contamination focused on cotton fabrics contaminated with liquid pesticides. Only a few recent research articles reported the effectiveness of chemical resistant glove cleanup after they were exposed to granular terbufos for 3 minutes or 30 minutes (Guo et al., 1997; Stone et al., 1997). The effectiveness of laundering for reducing pesticide residues in glove materials with different cleanup methods and laundry parameters is unknown.

The objectives of this study were 1) to determine the effects of various exposure times and pesticide composition on contamination levels and breakthrough times of nitrile, neoprene, and barrier laminate glove materials exposed to granular pesticides and 2) to determine the effects of experimental cleanup methods and laundry parameters on reduction of contamination by granular pesticides.

# CHAPTER 2. LITERATURE REVIEW

This chapter reviews literature regarding the pesticide contamination and decontamination of protective clothing and glove materials. The literature review contains the following four sections: pesticide exposure and assessment, test methods for resistance of chemical protective clothing materials, contamination and permeation of chemical protective clothing materials, and decontamination of protective clothing materials. On the basis of the literature review, 16 hypotheses were developed for this research study.

## Pesticide Exposure and Assessment

### Hand Exposure

Several studies on pesticide exposure in agriculture found that hands received the largest dermal exposure. Abbott (1984) reported that 97% of the dermal exposure occurred through the skin of the hands and forearms. In another study about the exposure of commercial pesticide applicators to the herbicide alachlor (Scanderson, Ringenburg, & Biagini, 1995), researchers found that the skin of hands was frequently exposed to pesticides. Zweig et al. (1985) investigated the dermal exposure of strawberry harvesters to carbaryl. In this study, dermal exposure of a group of eighteen strawberry harvesters to carbaryl was monitored during three consecutive workdays. The

result showed that the hands and lower arms of strawberry harvesters received the largest exposure to carbaryl while other parts of the body only had very low or nondetectable amounts of carbaryl.

**Passive Dosimetry**

In the field studies of pesticide exposure, passive dosimetry is one of the major approaches to estimating farm workers' potential exposure to pesticides. With passive dosimetry, absorbent patches are attached in protective clothing and worn by test subjects. Passive dosimetry can be used not only to estimate the amount of pesticide exposed on the skin but also to identify the routes of pesticide exposure.

Passive dosimeters are used as collecting media to monitor and measure farm workers' dermal exposure to pesticides (Cloud, 1988). Often they are composed of several layers of cotton gauze or alpha cellulose sheets and backed with a layer of aluminum foil or glassine paper to prevent penetration of pesticides. Some layers of cotton gauze usually are used for trapping particulate pesticide residues, while alpha cellulose sheets are used for absorbing gaseous and liquid pesticide residues. In a field study on dicofol exposure to citrus applicators, 4x4 inch squares of alpha cellulose pads backing a glassine paper were stapled to regular work clothing as collecting media to monitor pesticide exposure (Nigg, Stamper, & Queen, 1986).

Numerous studies on estimating dermal exposure of farm workers to pesticide have been conducted using various types of dosimeter materials in the recent years (Cloud, 1988). However, because of the variety of dosimeter materials used and the lack of data on their effectiveness, it is difficult to interpret data and compare results among different studies.

Generally, the pesticide efficiency of dosimeters varies depending on their surface characteristics, porosity, shape, and size (Kirchner et al., 1996). In recent years, there has been increasing interest in investigating the effectiveness of different dosimeter materials. In a study on the evaluation of various dosimeter backing materials, Bhat and Perenich (1990) examined their effectiveness as barriers to pesticide penetration. Four fabrics were used as penetration barriers: 100% cotton woven fabric, coated Tyvek®, uncoated Tyvek®, and Barricade® non-woven fabrics. The fabric samples were backed with four different dosimeter materials: eight-ply cotton gauze, 100% cotton t-shirt, #42 Whatman filter paper, and alpha-cellulose. One ml of pesticide was applied to the fabric samples. A significant difference was found among four dosimeter materials: 8-ply gauze showed a lower level of penetration of pesticides than the other three dosimeter backing materials. Researchers concluded that alpha-cellulose, cotton t-shirt, and #42 Whatman filter paper may be used as dosimeter materials to detect the penetration of pesticide through the fabrics.

## Test Methods for Resistance of Chemical Protective Clothing Materials

### Penetration and Permeation

After exposure, pesticides may remain on the surface of glove materials or move through glove materials by penetration and/or permeation. Penetration is "the flow of a chemical through closures, porous materials, seams, and pinholes or other imperfections in a protective clothing material on a nonmolecular level" (American Society for Testing and Materials, 1997a, pp. 825). When penetration occurs, the challenge chemical moves through holes in the material.

Permeation means that "a chemical moves through a protective clothing material on a molecular level" (American Society for Testing and Materials, 1997b, pp. 816). Permeation is caused by a chemical concentration gradient across materials. Permeation includes three steps. (1) Molecules of the chemical are sorbed into the exposed surface of the materials. (2) The sorbed molecules diffuses through the materials. (3) The molecules desorbs from the inside surface.

### Standard Test Methods

In laboratory studies of chemical penetration and permeation, the major approach has focused on the methods for evaluating resistance of chemical resistant gloves to permeation by liquid pesticides (Ehntholt et al., 1990; Jencen & Hardy,

1988, 1989; Moody & Ritter, 1990). One standard method of testing glove efficacy (American Society for Testing and Materials, 1997a) is the ASTM F 903-96. This testing method is used to evaluate penetration resistance of glove materials. It employs a pressurized cell to hold the specimen of glove materials and relies on visual detection the chemical penetration through the glove materials.

The ASTM F 739-96 standard test method for resistance of protective clothing materials to permeation by liquids and gases under conditions of continuous contact is a commonly accepted method for measuring chemicals permeation (American Society for Testing and Materials, 1997b). This method uses a standard cell and a liquid or gaseous collection medium. ASTM F 739-96 determines both breakthrough time and the steady state permeation rate. The breakthrough time is the elapsed time between initial contact of the test chemical with the outside surface of a protective clothing material and the time at which the chemical is detected at the inside surface of the material by means of the chosen analytical technique. The steady state permeation rate refers to the constant rate of permeation after breakthrough when all forces affecting permeation have reached equilibrium. ASTM method F 739-96 allows use of either a liquid or gas as collection medium. This method recommends distilled water as a collection medium when simulating perspiration on the inside surface of a glove material specimen and recommends

nitrogen or helium as a collection medium when simulating air on the inside surface of the specimen.

**Collection Medium**

In recent years, an increasing number of research studies have appeared on permeation testing performed by the standard test procedures and with different collecting media. Fricker and Hardy (1992) investigated the permeation characteristics of glove materials by organic solids such as quinone, camphor, phenol, naphehalene, and p-nitro-toluene. In this study, helium was used as a collecting media. Gaseous helium flowed through a stainless steel cell and contacted with the back of specimens of glove materials; then the collecting medium exited from the cell and was injected into a GC column for quantitative analyses. In general, gas, such as nitrogen or helium, is considered as a good collection medium because of its high solubility properties. However, it may not simulate accurately the permeation characteristics of glove use.

To simulate practical use of gloves, some aqueous liquid media have been used as collection medium. Fricker and Hardy (1994) used a saline solution as a collection medium to investigate the permeation characteristics of organic solids through protective glove materials. The result showed that the saline-based collection method usually generated longer breakthrough time and lower steady state permeation rate (SSPR) than the method using helium collection media. The authors

concluded that the polarity of the glove materials might be a reason that causes the decrease of measured permeation rate. In a study about relative rates of solvent and solute penetration through protective glove materials (Watkinson et al., 1993), distilled water was used as the collection medium for measuring the permeation of cyclohexanone; mixture of ethanol and water (50/50 by volume) was used for evaluation involving p-xylene as permeant because of the low water solubility of p-xylene.

Although water or a gas can be used as the effective collection media in experiments involving volatile or water soluble permeants, they may be inappropriate as collection media for many pesticide formulations in which the active ingredients are neither water soluble nor volatile (Ehntholt et al., 1990). Thus, it is important to select a collection medium that would efficiently absorb or solubilize a low volatility, low water solubility active ingredient permeant. Some organic solvents or mixtures of solvent and water have been used as the collection medium for the evaluation of glove permeation properties. However, these methods suffered from limitations because some solvents might have interaction with glove materials that could alter permeation characteristics of glove materials.

As an alternative, a solid collection medium has been used to test the permeation of low water solubility, low volatility active ingredients through glove materials. Ehntholt et al. (1990) used a thin (0.02 in. thick) sheet of silicone rubber as solid collection medium to collect low volatility, low water

solubility permeants. In their study, permeation tests were conducted with ten commercially available protective glove materials and six concentrated pesticide formulations. The results of the study indicated that silicone rubber collection materials can be used to test the permeation of low water solubility, low volatility active ingredients through glove materials. However, the collection method was less useful for evaluating the permeation of active ingredients with relatively high water solubility. For water soluble active ingredients, water is usually considered as the best collection medium. Thus, it is important to select an appropriate collection medium for specific pesticide formulations of interest.

## Contamination and Permeation of Chemical Protective Clothing Materials

Factors affecting the permeation properties of glove materials include temperature, the thickness of glove materials, the chemical composition of glove materials, and the chemical composition and the formulation of pesticides (Raheel, 1994).

### Temperature and Glove Material Thickness

In general, as temperature rises, permeation rates increase, while breakthrough times decrease. The thickness of glove materials is a critical factor determining the permeation process of glove materials (Jencen & Hardy, 1989; Schlatter & Miller, 1986). The permeation of a solvent and/or active

ingredient through glove materials is closely related to the diffusion of that solvent and/or active ingredient in glove materials. Jencen and Hardy (1989) examined the effect of glove material thickness on permeation characteristics. Four different thicknesses of neoprene glove materials and five thicknesses of natural rubber were examined against different solvents. The researchers found that there was a linear relationship between the square root of the breakthrough time and thickness. In general, this means that the greater glove thickness, the longer the breakthrough time. In addition, researchers found that the steady state permeation rate was related inverse-linearly to thickness. The greater the glove thickness, the less the exposure to the chemicals.

**Glove and Pesticide Chemical Composition**

The permeation resistance of glove materials to pesticides is related to glove materials, and to chemical composition and formulation of pesticides. In the past decade, research has examined permeation resistance of different glove materials to various pesticides. Most investigation focused on the various pesticide formulations that contain organic solvents or in which the active ingredient itself was an organic solvent. Schwope et al. (1992) examined the permeation resistance of 13 different glove materials to approximately 20 pesticide formulations, which included 10 active ingredients and 10 carrier solvents. The researchers simultaneously monitored the permeation of the

carrier solvents and active ingredients and found that the carrier solvent usually permeates earlier and at a higher permeation rate than the active ingredient. Results of the study showed 13 glove materials had different permeation resistance to pesticide. Nitrile rubber, butyl rubber, and plastic film laminate glove materials were most resistant to permeation, while natural rubber and polyvinyl chloride glove materials were least resistant. Similarly, Ehntholt et al. (1990) examined the permeation resistance of ten commercially available glove materials to ethyl parathion and meta-xylene using a modified standard cell. Results of the study indicated that nitrile rubber, butyl rubber, and Silver Shield® glove materials exhibited good permeation resistance, while natural rubber and polyethylene glove materials exhibited very poor permeation resistance. In another study, Fricker and Hardy (1992) investigated glove material permeation resistance to organic solids. In their study, five different glove materials, natural rubber, PVC, urethane, nitrile, and neoprene, were evaluated against nine organic solids. The researchers reported that nitrile and neoprene generally exhibited the best permeation resistance.

**Glove Manufacturers**

In some cases, a variety of permeation resistance may exist for the gloves sold under the same generic name from different manufacturers since the formulations for the gloves sold vary

from manufacturer to manufacturer. Mickelsen and Hall (1987) investigated the differences in breakthrough time among glove materials under the same generic name produced by different manufacturers. Nitrile and neoprene gloves with the same nominal thickness were tested against three different chemicals. The researchers found that there was a significant difference in chemical breakthrough times among the same glove materials produced by different manufacturers. They suggested that the difference in chemical breakthrough times might be due to differences in chemical composition or in the fabrication process.

**Pesticide Formulation**

The pesticide formulation type is also a critical factor influencing permeation characteristics of chemical protective materials to agricultural pesticides. Pesticides are available in several different kinds of liquid and dry formulations. The granular formulation, one of the most widely used formulations in agriculture, is dry, ready-to-use pesticides. Most granules contain relatively low amounts of active ingredients, usually ranging from 1% to 20%. Granules are usually made by applying the active ingredient as aqueous solutions to various inert materials such as clay, corn cobs, or walnut shells (Sawyer, 1983). The granular formulations are considered to be relatively safe for use compared to liquid formulations. Many toxic pesticides are made by manufacturers in granular forms to

reduce the potential risk of farm worker exposure to toxic pesticides when they use these chemicals.

**Contamination of Clothing Fabrics and Gloves**

Braaten (1988) studied the contamination of cotton fabrics by granular aldicarb (Temik® 15G) when the fabrics were soiled with synthetic perspiration and synthetic sebum. In this study, soiled 5x5 cm fabric specimens were contaminated with 0.42 g granular Temik for different periods of time. The area of the pesticide contamination in a fabric specimen was about the size of a dime. The perspiration, sebum, and the contact time significantly influenced the contamination of fabrics by granular aldicarb. As the contact time increased, the amount of contamination of fabrics increased.

Stone et al. (1992a) reported the laboratory contamination methods of cotton fabrics with granular terbufos. The different amounts of granular terbufos (0.1 g or 0.5 g) were deposited directly on the 8x8 cm fabric specimens where the specimens were either starched or unstarched and either wet or dry. The contamination level of fabrics was closely related to the exposure time, contamination amount, time delay before extraction, and moisture content of the specimen. There were detectable pesticide residues in the specimens after the contaminated fabrics were exposed to flowing air for 72 hours.

Stone et al. (1995) investigated the contamination levels of three different glove materials after exposure to granular

terbufos for three minutes. The study showed that contamination levels of three different glove materials differed significantly and no detectable contamination was found in the gauze used to back specimens after a three-minute exposure.

### Decontamination of Protective Clothing Materials

Pesticide contamination on protective clothing may be reduced or removed by appropriate laundering procedures. Several researchers (Kim, Kadolph, & Stone, 1988; Laughlin & Gold, 1990; Laughlin, Newburn, & Gold, 1991; Raheel, 1987; Stone et al., 1993) have investigated decontamination of pesticide protective clothing. Decontamination of pesticide protective clothing was complex and was related to many variables (Laughlin & Gold, 1988; Laughlin, 1993). These variables included soil type, textile substrate characteristics, and decontamination factors. The type and formulation of pesticides, the pattern and time of pesticide exposure, and laundering factors such as water temperature, detergent, prerinsing, and relaundering may affect the reduction of pesticide contamination on protective clothing.

### Pesticide Chemical Composition

Pesticide chemical composition is one of the factors affecting the laundering effectiveness for reduction of pesticide contamination. The clean-up effectiveness of protective clothing may be pesticide-specific.

In a comprehensive summary of studies on the effectiveness of laundering in pesticide removal from clothing fabrics in six states of the U.S. and one province of Canada (North Central Agricultural Experiment Stations, 1988), seventeen pesticides were used to contaminate fabrics. A known amount of pesticide at 1.25% active ingredient was applied on the selected fabric specimens. The tested fabrics included 100% cotton, nylon, acrylic, olefin, and cotton/polyester blends. After fabric specimens were contaminated, specimens were laundered in a Launder-Ometer by using a 9 minute wash cycle, a 5-minute rinse, and another 3-minute rinse (American Association of Textile Chemists and Colorists, 1980). The results indicated that the percentage reduction of pesticide residue after laundering varied among the different pesticides. However, in this study, the pesticide amount applied to the specimens before laundering, fabric type and structure, and the laundering parameters and conditions also varied with the specific pesticides.

Keaschall, Laughlin, and Gold (1986) studied eleven pesticides from three chemical classes--organophosphates, carbamates, and organochlorines--to determine the effect of laundering procedures on removal of insecticides residues from fabrics. A 0.2 ml aliquot of emulsifiable concentrate pesticide solution was applied to the surface of three fabrics--unfinished, renewable consumer applied fluorocarbon finished, and commercially applied fluorocarbon finished fabrics. The results showed that there was a significant difference both

among and within pesticide classes in pesticide residue after laundering. Organochlorine insecticides had the largest residues in specimens, followed by organophosphates and carbamates. The comparison of different pesticides within the same pesticide classes indicated that organophosphate pesticides had the greatest variability in pesticide residue.

**Pesticide Formulation**

Pesticides used in agriculture production usually are a mixture of active ingredient and other carrier materials such as solvent, wetting agent, or powders (Bohmont,1990). Some formulations are ready to use, such as granular pesticide, but others must be diluted with a solvent or water before they are applied. Several different types of formulations, such as emulsifiable concentrate, wettable powders, flowables, dusts, and granules, may be used for one active ingredient. But, many pesticides are available only in a few formulations.

Pesticide formulations affect the efficiency of decontamination of clothing fabrics. In several studies on the effect of laundering procedures on decontamination of apparel fabrics (Easley, Laughlin, Gold, & Tupy, 1983; Laughlin, Easley, & Gold, 1985; Laughlin, Newburn, and Gold 1991), pesticide formulation was considered as one critical factor that affected the effectiveness of decontamination.

Easley, Laughlin, Gold, and Tupy (1983) investigated laundering procedures required to remove 2,4-D ester and 2,4-D

amine herbicide from contaminated fabrics. The contaminated fabric specimens were laundered by a 12-minute wash cycle with 150 ml detergent solution and two rinse cycles of 5 minutes and 3 minutes respectively in a Launder-Ometer. Laundering temperature was either a $60^0$C wash and $49^0$C rinse or a $30^0$C water wash and rinse. The results showed that 99.17% to 99.65% of 2,4-D amine was removed from contaminated fabrics after laundering; but laundering procedures only removed 28.86% to 44.99% 2,4-D ester herbicide. Researchers concluded that differences in the amount of 2,4-D herbicide removed from contaminated fabrics were due to pesticide formulation; water solubility of the formulation was a major factor affecting effectiveness of pesticide removal through laundering.

In another study, Laughlin, Easley, and Gold (1985) compared the pesticide residue in fabrics contaminated with methyl parathion (MeP) in emulsifiable concentrate, wettable powder, and encapsulated formulations after laundering in a Launder-Ometer using a modified AATCC test method 61-1980 (American Association of Textile Chemists and Colorists, 1980). Residues in fabrics were greater for emulsifiable concentrate formulation, while wettable powder and encapsulated formulations MeP residues were lower. Researchers suggested that residues from emulsifiable concentrate were more difficult to remove through laundering because oil-based emulsifiable concentrate formulations had an affinity for oleophilic polyester fibers. A study done by Laughlin, Newburn, and Gold (1991) obtained

similar findings. They examined effective laundry methods for the removal of the pyrethroid insecticides, cyfluthrin and cypermethrin of wettable powder (WP), and emulsifiable concentrate (EC) formulations from fabrics. The cypermethrin residues from either EC or WP after laundering were lower than cyfluthrin. The cyfluthrin EC formulation residues remained greater in fabrics after laundering than WP formulation. Laughlin et al. concluded that pesticides formulated as an oil-base concentrate were more difficult to remove from fabrics. In general, an oil-based concentrate pesticide can enter the inside of fibers more easily than a water-based pesticide. Obendorf and Solbrig (1986) observed the distribution of malathion and methyl parathion residues on cotton/polyester contaminated fabrics by electron microscopy. They found that pesticide not only distributed on the surface of fibers but also entered the inside of fibers before laundering. It was easier to remove the pesticide residues from the surface of fibers through laundering than from in the inside of fibers.

Raheel (1987) studied laundering variables in removing carbaryl and atrazine residues from contaminated fabrics. Fabric specimens were contaminated with carbaryl and atrazine of wettable powder and flowable liquid formulations. The contaminated fabric swatches were laundered for 9 minutes and rinsed twice for 5 minutes and 3 minutes respectively in a Launder-Ometer. Two laundering temperatures, $49^0$C and $60^0$C and two types of detergents--phosphate powder detergent and nonionic

heavy duty liquid detergent--were used for this study. No significant differences were found between two different formulations in pesticide residues in fabrics after laundering.

**Pesticide Solubility**

Pesticide solubility may play a role in decontamination of fabrics. Different pesticides have different water solubility. Several researchers (Easley et al., 1983; Laughlin et al., 1985) suggested that the water solubility of the active ingredient might be a more reliable indicator than chemical class in terms of the effectiveness of pesticide removal after laundering.

Easley et al. (1983) reported that 2,4-D amine herbicides were removed more easily from fabrics by laundering than 2,4-D ester herbicides; this was attributed to the insolubility of 2,4-D ester in water and the relative higher solubility of 2,4-D amine. These results are supported by the findings of Laughlin et al. (1985). They found that the emulsifiable concentrate was more difficult to remove from fabrics than wettable powder and encapsulated formulations because emulsifiable concentrate had lower water solubility. However, the effectiveness of pesticide removal was not always a function of pesticide solubility. Researchers (North Central agricultural Experiment Stations, 1988) suggested that formulation might affects pesticide removal more than solubility.

**Pesticide Concentration**

Pesticide concentration is another factor in residue removal from contaminated fabrics after laundering. Laughlin et al. (1985) examined the effect of pesticide concentration on decontamination of methyl parathion from fabrics. Five concentration levels--0.25%, 0.5%, 1%, 2%, and 54%--were used to contaminate 100% cotton and 50/50 cotton-polyester denim fabrics. After contamination, fabric specimens were washed at $60^0$C and rinsed twice at $49^0$C. The results showed that as initial pesticide concentration increased, pesticide residues in fabrics increased after laundering; higher concentrations, such as 54%, were difficult to remove with one laundry cycle, but lower concentrations were more easily removed.

**Water Temperature**

Water temperature is an important laundering variable that influences the removal of pesticides from clothing materials. Several researchers (Easley et al., 1982; Easter, 1983; Lillie et al., 1981, 1982) found that as water temperature increased, the residue of pesticide removed increased. Lillie et al. (1981) investigated the effects of wash water temperature on decontamination of 100% cotton fabrics. The fabric specimens were contaminated with diazinon, propoxur, chlordane, malathion, and bromacil. Results of the study indicated there was a tendency for the higher water temperature to increase the removal of pesticides from the fabrics except for chlordane. A

study about methyl parathion removal from work-weight fabrics by laundry procedures was conducted by Easley et al. (1982). These researchers reported that there was less removal of MeP at 30$^0$C than at 60$^0$C. There was an interaction between water temperature and laundry detergent. Heavy duty liquid (HDL) detergent helped to remove more MeP from the fabric at higher water temperature.

Although more residue removal with increased water temperature was often reported, other researchers (Kim et al., 1982) reported that water temperature did not significantly influence the removal of fonofos residues from light weight fabrics. In another study (Kim et al., 1986) about the removal of alachlor residues from clothing fabrics by laundry, researchers found that there was no significant difference in removal of alachlor residues between hot wash (60$^0$C) and warm wash (49$^0$C). Similar findings were reported by other researchers (Olsen et al., 1986; Raheel, 1987).

**Detergent**

Detergent is also an important laundering variable that influences the removal of pesticides from protective clothing materials. In general, washing with detergent removes more pesticide residues in fabrics than did washing without detergent (Laughlin, 1993). Kim et al. (1982) found that there was a significant difference in residue removal from both the light and heavy fabrics between laundering with detergent and without

detergent. The pesticide residues after laundering with detergent were lower than those after laundering by water alone. Laughlin et al. (1993) summarized the studies of pesticide residue removal in laundering and concluded that laundering with detergents could reduce pesticide residues in fabrics more effectively than laundering with water alone.

The effect of detergent type on the removal of pesticide residues has been reported (Kim et al., 1986, 1988; Popelka, 1985; Raheel, 1987). Kim et al. (1986) reported that phosphate detergents improved the removal of alachlor from light weight fabrics, while in heavy fabrics there was no significant difference among three different types of detergents (AATCC, Tide®, heavy-duty liquid). In a study about the effect of laundering factors on the residue removal of fonofos from clothing fabrics, Kim et al. (1988) examined the effectiveness of three types of detergents (no detergent, household phosphate, AATCC) in the removal of fonofos. The household phosphate detergent was more effective in the removal of fonofos than the other two treatments; but there was no significant difference in the removal of fonofos residues between the no detergent and the AATCC type. This finding was consistent with that of Popelka (1985). Raheel (1987) investigated the efficacy of laundering variables such as detergent type in the removal of carbaryl and atrazine residues from contaminated fabrics. She found that heavy duty liquid detergent (HDL) was more effective than

powdered detergent (Tide®) in reducing pesticide residues from DP-finished polyester/cotton fabrics.

**Cleanup of Chemical Resistant Glove Materials**

In contrast to the cleanup of clothing fabrics, little information is available in the literature on decontamination of chemical resistant glove materials by laundering. Stone et al. (1995) investigated the effects of experimental washing with water and detergent on the removal of pesticide residue from three different types of glove materials exposed to granular terbufos (Counter® 15G).

In this study, two methods--the glove-finger method and the petri-dish method--were used to contaminate glove specimens. With the glove-finger method, a glove finger specimen was cut off, mounted over a test tube, and then pushed into a beaker of granules for 3 minute exposure. With the petri-dish method, a 6x6 cm square glove specimen was backed with gauze and attached by means of tape. Terbufos granules (0.05 g) were placed over the 4x4 cm contamination area in the center of the specimens in a covered petri dish for a 30-minute exposure. After exposure, the contaminated specimen was trimmed into a 4x4 cm square. The specimens were washed by stirring in a beaker of 150 ml detergent solution for three minutes.

The study showed that with a three-minute exposure to granular terbufos by glove-finger methods, after the experimental washing, residues of terbufos were reduced by 67%

for nitrile glove and 30% for neoprene gloves and were not reduced significantly for barrier laminate gloves. However, with a 30-minute exposure to granular terbufos by petri-dish methods, the simple washing did not decrease the terbufos residues significantly in nitrile, neoprene, and barrier laminate glove materials specimens. In another similar study on the effectiveness of three different laundering methods for decreasing terbufos contamination in nitrile glove materials, Guo et al. (1997) reported that the simple laundering processes including wash or flush or their combination have little effect on the removal of terbufos residues from nitrile glove specimens after a 30-minute exposure by petri dish methods.

## Research Hypotheses

On the bases of literature review, the following hypotheses were developed for this research study:

Hypothesis 1: There are no significant differences in contamination levels and breakthrough time of glove materials exposed to granular terbufos at different exposure times.

Hypothesis 2. There are no significant differences in contamination levels and breakthrough time among different glove materials exposed to granular terbufos.

Hypothesis 3: There is no interaction effect between glove material and exposure time on contamination levels and breakthrough time of glove materials exposed to granular terbufos at different exposure times.

Hypothesis 4: There are no significant differences in contamination levels and breakthrough time of glove materials exposed to granular tefluthrin at different exposure times.

Hypothesis 5. There are no significant differences in contamination levels and breakthrough time among different glove materials exposed to granular tefluthrin.

Hypothesis 6: There is no interaction effect between glove material and exposure time on contamination levels and breakthrough time of glove materials exposed to granular tefluthrin at different exposure times.

Hypothesis 7: There are no significant differences in contamination levels and breakthrough time of glove materials exposed to granular terbufos and tefluthrin.

Hypothesis 8: There are no significant differences in the terbufos residues in glove materials among different cleanup treatments.

Hypothesis 9: There are no significant differences in the tefluthrin residues in glove materials among different cleanup treatments.

Hypothesis 10: There were no significant differences between the amount of pesticide residues found in flushing water solution and that in washing water solution.

Hypothesis 11: There are no significant differences in the amount of terbufos residues in glove materials after laundering with the use of detergents and without detergents.

Hypothesis 12: There are no significant differences in the amount of terbufos residues in glove materials after laundering at different laundering temperatures.

Hypothesis 13: There are no significant differences in the amount of tefluthrin residues in glove materials after laundering with the use of detergents and without detergents.

Hypothesis 14: There are no significant differences in the amount of tefluthrin residues in glove materials after laundering at different laundering temperatures.

Hypothesis 15: There are no significant differences in the amount of pesticide residues in laundering water solution with the use of detergents and without detergents.

Hypothesis 16: There are no significant differences in the amount of pesticide residues in laundering water solution between different laundering temperatures.

# CHAPTER 3. MATERIALS AND METHODS

This chapter presents the materials and methods used in this study. First it discusses materials. Secondly it outlines variables, research design, three experiments, extraction of pesticide residue, gas chromatography, data collection, and data analysis. This research was an experimental study. The lack of any standard test methods caused this research to be conducted based on methods previously reported in the cited literature (Guo et al., 1997; Stone et al., 1997). The work sequentially was divided into three primary experiments. Experiment 1 investigated the effects of exposure times and pesticide composition on contamination levels and breakthrough times of nitrile, neoprene, and barrier laminate glove materials exposed to granular pesticides. Experiment 2 examined the effects of cleanup methods on reduction of contamination in glove materials. Experiment 3 investigated the effects of water temperature and detergent on reduction of contamination in glove materials. Finally, four pilot studies used for guiding the development of methods are introduced in this chapter.

## Materials

### Pesticides

The granular pesticides used in this study were terbufos (Counter® 20CR) and tefluthrin (Force® 3G) because of their

widespread use in Iowa and the United States as previously noted. They were obtained from an Iowa State University research farm from lock and load storage containers of pesticides. Terbufos was made by American Cyanamid Co., Wayne, New Jersey and tefluthrin by Zeneca Inc., Wilmington, Delaware. The pure analytical reagent standards of terbufos and tefluthrin respectively were obtained from the same manufacturers and used to prepare primary standards of the pesticide.

Terbufos is highly toxic and has a "Danger" label. It can be absorbed rapidly through skin. Repeated and prolonged skin contact may result in progressively increased susceptibility to poisoning. If swallowed, inhaled, or absorbed through the skin, terbufos may be fatal. Compared with terbufos, tefluthrin is relatively safe. It has a "Caution" label and is classified as slightly toxic. However, according to reports from the staff of the agricultural extension service of Iowa State University, some Iowa farmers complained of skin irritation and sensitization after they handled granular tefluthrin. Some characteristics of terbufos and tefluthrin are shown in Table 1. The structural formulas of terbufos and tefluthrin are drawn in Appendix A (Farm Chemicals Handbook, 1993).

**Gloves**

The glove materials used in this study were nitrile, neoprene, and barrier laminate. Nitrile gloves (Sol-Vex®) were donated by Ansell Edmont Industrial Inc., Coshocton, Ohio.

Table 1. Terbufos and Tefluthrin Characteristics

| | Terbufos | Tefluthrin |
|---|---|---|
| Family | Organophosphate | Synthetic pyrethroid |
| Action | Systemic insecticide | Insecticide, acaricide |
| Melting point | 29.2$^0$C | 49.2$^0$C |
| Solubility | In water 15 ppm | In water 4 ppm |
| Molecular formula | $C_9H_{21}O_2PS_3$ | $C_{23}H_{19}CLF_3NO_3$ |
| Molecular weight | 288.43 | 449.86 |
| Toxicity[a] | 4.5 mg/kg | 79 mg/kg |

[a] Oral $LD_{50}$ in male rats Tech

Neoprene™ gloves were purchased from Lab Safety Supply Inc., Janesville, Wisconsin, and were made by Ansell Edmont. Barrier laminate (Silver Shield®) gloves were obtained from North Safety Products, Charleston, South Carolina.

Researchers and experts in selecting protective clothing recommended nitrile, neoprene, and barrier laminate gloves for agricultural pesticides operations based on their physical characteristics and chemical resistant properties (United States Environmental Protection Agency, 1993). Gloves of these materials were used frequently by farm workers. The construction features of the gloves used in this study are

characterized in Table 2. The structural formulas of the glove materials are drawn in Appendix A (Dean, 1987).

**Other Materials**

A RESPREP™·C18·47 disk and a Swinnex disc filter holder were used for the solid phase extraction of pesticide residues

Table 2. Glove Characteristics

| Glove | Character | Gauge (mm) | Weight ($g/m^2$) |
|---|---|---|---|
| Nitrile | Hand mold; dipped in polymer for hand shape | 0.381 | 441.51 |
| Neoprene | Hand mold; dipped in polymer for hand shape | 0.432 | 912.88 |
| Barrier laminate | Flat, hand print design with sealed edges | 0.076 | 56.67 |

from laundering water solutions. The disk was obtained from RESTEK Corporation, Bellefonte, Pennsylvania, and the disc filter holder from Millipore Corporation, Bedford, Massachusetts.

The RESPREP™·C18·47 disk consists of a glass fiber embedded with bonded silica. The capacity of a RESPREP™·C18·47 disk is approximately 30 mg for a well-retained compound. A RESPREP™·C18·47 disk can process sample volumes of 1 liter or

more. Typical extraction procedures can be run at flow rates from 50 to 500 ml per minute.

Alpha-cellulose sheets were used as collection media. They were donated by Rayonier Corporation, Jesup, Georgia. Thickness of sheets is 1.1 mm and weight of sheets is 901.2 $g/m^2$. Ethyl acetate of pesticide grade was used for extracting terbufos residues from glove specimens and alpha-cellulose pads and iso-octane of pesticide grade for extracting tefluthrin residues from glove specimens and pads. The two solvents were obtained from Fisher Scientific, Fair Law, New Jersey.

The detergent used in this study was liquid Tide® because a survey of Iowa farm family on laundering pesticide-soiled clothing have shown that Tide® is a commonly used brand (Stone, Koehler, Kim, & Kadolph, 1986). It was made by Procter & Gamble, Cincinnati, Ohio, and was purchased from a local grocery store. Its ingredients include anionic and nonionic surfactants and enzymes. E-Pure® ultra pure water was used for flushing, washing, and rinsing glove specimens.

Between uses, all glassware used in this study was rinsed with acetone and then was washed and rinsed three times with E-Pure® water. After rinses with solvent and water, the glassware was cleaned on the clean cycle in a conventional electric self-cleaning oven at $450^0C$ for 4 hours to volatilize any remaining pesticide residues. If necessary, the glassware was rinsed with E-Pure® water to remove inorganic residue after the clean cycle.

## Variables

This study had six independent variables. They were respectively pesticide, glove material, exposure time, laundering method, wash water temperature, and detergent. The dependent variables were the amount of pesticide residue in the glove materials, alpha-cellulose pads, and laundering water solution.

## Research Design

The study was divided into three separate experiments. The first experiment investigated the effect of pesticide composition and exposure time on contamination levels and breakthrough times of three different glove materials exposed to granular pesticide to test null hypothesis one through null hypothesis seven. The second experiment investigated the effect of experimental cleanup methods on reduction of contamination by granular pesticides to test null hypotheses eight through ten. The third experiment investigated the effect of laundry parameters on reduction of contamination by granular pesticides to test null hypothesis eleven through null hypothesis sixteen. In all the experiments, each treatment method had three replicates. In addition, a control specimen (no exposure of pesticides) for each type of glove material and alpha-cellulose pads was employed to determine whether glove materials and pads had been contaminated accidentally before experimentation. Specimens were assigned randomly to treatments.

## Experiment 1

A 2x3x6 factorial design was used for experiment 1. Granular terbufos and tefluthrin were used for this experiment. Three types of glove materials were used: nitrile, neoprene, and Silver Shield®. Three replicate specimens were prepared for each glove material. Six exposure times were used: 1 hour, 2 hours, 4 hours, 8 hours, 16 hours, and 24 hours.

### Glove Specimen Preparation

The 6x6 cm square specimens were cut from three different types of gloves. A 4x4 cm square in the center of the glove specimen face was marked as an area of contamination using a marking pen. Alpha-cellulose sheets were cut into 6x6 cm square pads. Aluminum foil was cut into 7x7 cm square pads. A glove specimen was backed together with an alpha-cellulose pad specimen so that the outside of the glove material was exposed while the inside contacted the alpha-cellulose pads. These two layers were placed on aluminum foil and edges of the foil were folded in 0.5 cm. Then the "sandwich" structure was taped on the edges to prevent air flow around the sides to the pads. This helped insure that all pesticide residues found in the pads was from permeation rather than from volatile fumes (See diagram in Appendix B). Before contamination, specimens were conditioned in constant conditions of 21± 1$^0$C and 65 ± 2% for 24 hours to bring them into comparable moisture content which could theoretically affect chemical absorption.

**Glove Specimen Contamination**

The contamination of glove specimens was conducted under a fume hood for the health of researchers. Three hundred milligrams of terbufos or tefluthrin granules were weighed with a foil weighing dish and an electronic balance for each specimen. An alpha-cellulose and foil backed glove specimen was placed in a clean petri dish. Granular pesticide (0.3 g) was sprinkled as evenly as possible by a spatula onto the 4x4 cm square contamination zone of glove specimens. The petri dish was covered and the specimen was exposed to granular pesticides for the specific time the experimental design determined. After exposure, specimens were tipped to make granular pesticides roll off the specimens into a pesticide waste container. All visible granules were removed from the specimens by a spatula. The entire 6x6 cm specimen was held with tweezers and was trimmed to 4x4 cm square using a scissors along the previously marked lines. Glove specimens were separated with tweezers from alpha-cellulose pads and foil; then glove specimens and alpha-cellulose pads were placed respectively in separate labeled test tubes with a screw cap containing 25 ml of extraction solvents for a 24-hour extraction time.

**Experiment 2**

A 2x3x2x3 factorial design was used for experiment 2. Two pesticide treatments and three glove material treatments were the same as in the first experiment. The two exposure times

were 3 minutes and 30 minutes. Three treatments were used in this experiment. A control set of specimens was contaminated but not laundered for purposes of comparison. The first cleanup method flushed contaminated specimens with water. In this study, the flush was defined as a sudden flow of water to rinse and clean glove specimens exposed to granular terbufos and tefluthrin. The second cleanup method used the Launder-Ometer to wash and rinse contaminated glove specimens.

**Glove Specimen Preparation and Contamination**

In experiment 2, protocol of glove specimen preparation and contamination were basically the same as in the first experiment. There was only a minor revision of the protocol. Flat 6x6 cm square glove specimens were backed with 7x7 cm square foil rather than alpha-cellulose pads. The edges of the foil were folded in 0.5 cm and taped at the edges. In this experiment, the collection media--alpha-cellulose pads--were no longer employed because the results of previous experiments indicated that granular pesticides did not permeate or penetrate glove materials during a 30-minute exposure time period.

**Glove Specimen Cleanup**

**Flush.** A 200 ml separatory funnel was filled with 150 ml of E-Pure® ultra pure water. The contaminated 6x6 cm specimens were trimmed to 5x5 cm using a scissors and tweezers. The specimens were separated from the backed foil. The foil was discarded

into a waste container. An edge of the specimen was held by a tweezers underneath the open end of the separatory funnel filled with the water solution directly from the water purification system. Water temperature was not controlled but was consistent with ambient room temperature and was about 21$^0$C. The 150 ml of flush solution was released from the separatory funnel and the contaminated face of specimens was flushed about 30 seconds. The flushed specimens were dried under a hood. After the flushed specimens were dry, the specimens were placed individually into 25 ml of extraction solvent in separate test tubes for 24 hours. The flush solutions were poured into labeled 200 ml jars with a screw cap and kept in a refrigerator at 4$^0$C until the time for extraction.

**Launder-Ometer**. An ATLAS LP2 Launder-Ometer® was used for glove specimen laundering. The contaminated 4x4 cm glove specimens were put in standard metal canisters and laundered for 9 minutes at 60$^0$C with 150 ml E-Pure® ultra pure water, 0.2 ml Liquid Tide® detergent, and 20 steel balls. After laundry, 150 ml of the laundering water solution was poured into a 200 ml jar and kept in a refrigerator at 4$^0$C until the time for extraction; after laundering, the 4x4 cm laundered glove specimens each were rinsed for 3 minutes and again for 2 minutes at 49$^0$C with 150 ml E-Pure® ultra pure water and 20 steel balls. After rinsing, the specimens were taken out of metal canisters and dried under a

hood. When specimens were dry, the specimens were put into 25 ml of extraction solvent in a test tube for 24 hours.

## Experiment 3

A 2x3x2x2 factorial design was used for experiment 3. Two pesticide treatments and three glove material treatments were used once again. Two laundering temperatures were 30$^0$C and 60$^0$C. Two detergent treatments were liquid Tide® detergent and wash water alone.

In experiment 3, the procedures for glove specimen preparation and contamination were basically the same as in the second experiment, except that only one exposure time, 30 minutes, was used. In this experiment, only one laundering method, Launder-Ometer laundering, was used. The protocol of glove specimen laundering was basically the same as in the Launder-Ometer laundering of the second experiment. In comparing high and low water temperature laundering, the high temperature specimens were laundered for 9 minutes at 60$^0$C with 150 ml of water and 0.2 ml of detergent or 150 ml of water alone and then rinsed for 3 minutes and again for 2 minutes respectively at 49$^0$C with 150 ml E-Pure® ultra pure water. For the low-temperature laundering, the glove specimens were laundered for 9 minutes and rinsed once for 3 minutes and again for 2 minutes at 30$^0$C.

## Extraction of Pesticide Residue

### Glove Specimens and Alpha-cellulose Pads

Terbufos residues in the contaminated, flushed, and laundered glove specimens, as well as alpha-cellulose pads, were extracted with ethyl acetate. Tefluthrin residues in the glove specimens and alpha-cellulose pads were extracted by iso-octane. After the 24-hour extraction period, the glove specimens or alpha-cellulose pads were taken out from the respective test tubes. The test tubes containing unknown quantities of pesticide and 25 ml of extraction solvent were kept in a refrigerator at $4^0$C until time for the GC analysis.

### Laundering Water Solution

Solid phase extraction techniques with ethyl acetate were used to extract the pesticide residues in flush or laundering water solution. A RESPREP™·C18·47 disk was properly inserted inside of a Swinnex disc filter holder and kept wrinkled side up. The filter holder was tightened by hand to avoid a possible leakage of liquid during extraction. Ten milliliters of methanol was sucked into a 60 ml plastic syringe. The plastic syringe with 10 ml of methanol was then connected with the inlet of a RESPREP™ disk. The disk first was conditioned by forcing 10 ml of methanol in a syringe through the disk by pushing syringe handles down. With the same methods, the disk again was conditioned by 10 ml of E-pure® ultra pure water; then, the

flush or laundering water solutions (150 ml) were forced through the disk for about 3 minutes by a positive pressure produced by pushing the syringe handles down. The disk was taken out from filter holders and dried under a hood for 5 minutes. Finally, the dried disk containing pesticide was put back inside the filter holders and eluted with 10 ml of ethyl acetate. The eluted solvent was kept in a test tube with a Teflon lined screw cap in a lab refrigerator until the GC analysis.

## Gas Chromatography

Two gas chromatographs were used for this study. A Varian 3400 gas chromatograph with a thermionic N.P. selective detector was used for the terbufos analysis. A Packard 427 gas chromatograph with an electron capture detector was used for the tefluthrin analysis. The parameters of gas chromatography are shown in Table 3.

## Data Collection

In the residue analysis of terbufos by Varian 3400 gas chromatography, the nanogram level of analytical standards of terbufos was used as the basis for calculating pesticide amount in the sample. Peak areas were used to measure the amount of terbufos in samples. In the residue analysis of tefluthrin by a Packard 427 gas chromatography, the $10^{-2}$ nanogram level of analytical standards of tefluthrin was used because the electron capture detector of that GC was highly sensitive to tefluthrin.

Table 3. Gas Chromatograph Parameters

| | Varian 3400 | Packard 427 |
|---|---|---|
| Detector | TSD (thermionic N.P. selective detector) | ECD (electron capture detector) |
| Column | 3% OV-17, 2 m x 1/4" x 2 mm i.d. | 1.5% OV-17, 1.95% OV-210, 4% SE30, 6% QF1; 6 ft x 3 mm i.d. |
| Column temperature | | 205°C |
| Initial | 160°C | |
| Final | 240°C | |
| Injector temperature | 240°C | 225°C |
| Detector temperature | 300°C | 275°C |
| Carrier gas | Nitrogen | Nitrogen |
| Flow rate | 35 ml/min | 35 ml/min |

Peak height was used to measure the amount of tefluthrin in samples.

Three different volumes of pesticide standards were injected into the GC and run. Thus, three corresponding peak areas or peak heights were obtained from the output of integrator of the GC. A linear curve of terbufos or tefluthrin was plotted using corresponding peak area or peak height as y-axis values and corresponding injected volumes as x-axis values using least square regression methods. The amount of pesticides in each specimen was calculated from the recorded peak heights

or peak areas per injection through the standard curve. Pesticide standards were run after every five sample injections.

Two GC injections were run per replication. They agreed within 3% or an additional injection was made. In the analysis of terbufos, an aliquot of the extracts obtained from neoprene and barrier laminate glove specimens were injected directly into the GC. The extracts obtained from nitrile glove specimens, alpha-cellulose pads, and flush and laundering water solution needed to be concentrated to stand within the concentration range of the analytical standards. An aliquot of these concentrated solutions then was injected into the GC. In the analysis of tefluthrin, most of the extracts obtained from glove specimens and alpha-cellulose pads required dilution. However, some extracts obtained from glove specimens, alpha-cellulose pads, and flush and laundering water solution still needed to be concentrated; others were directly injected into the GC.

**Data Analysis**

The peak area or peak height values per GC injection were used to calculate the values of pesticide residue in a 16 cm square specimen. The computation was based on standard curves and conversion formulas (Stahr, 1991). Finally, that value was divided by sixteen and converted into the amount of pesticide residues per cm square specimen. Six values in each treatment cell were reported and their mean was used as the pesticide residue amount ($ng/cm^2$) in a specimen.

Factorial analysis of variance was used to determine statistical difference 1) in pesticide contamination levels among different exposure times, glove materials, and pesticides to test hypothesis one through hypothesis seven, 2) in the amount of pesticide residues in glove materials and in laundering water solution among different laundering treatments to test hypothesis eight through hypothesis ten, and 3) in the amount of pesticide residues in glove materials and in laundering water solution between different laundering parameters to test hypothesis eleven through hypothesis sixteen. Post hoc multiple comparison also were used to identify further differences among the different levels of the factors. Linear regression was used to identify whether there was a linear relationship between pesticide contamination levels in three glove material specimens and exposure time (Myers & Well, 1991). Statistical analyses were conducted by SAS programs (SAS/STAT User's Guide, 1991). Significance levels were set at 0.05.

## Pilot Studies

The results of four pilot studies guided the development of methods to be used in the primary research. The purposes of these pilot studies were 1) to compare the effectiveness of cotton gauze with alpha cellulose pads as collection media to absorb pesticide residues that might break through glove materials, 2) to compare the contamination levels of glove materials exposed to Counter® 15G with Counter® 20CR, 3) to

compare the pesticide recovery rates of ethyl acetate with iso-octane as extraction solvent after glove materials were exposed to terbufos and tefluthrin, and 4) to determine the recovery rate of tefluthrin from water solution using solid phase extraction techniques.

**Pilot Study I**

Both cotton gauze and alpha cellulose sheets have been used as collection media to monitor pesticide exposure (Bhat & Perenich, 1990; Cloud, 1988), but the effectiveness of these materials as collection media to absorb residues of granular materials was unknown. The purpose of this pilot study was to compare the effectiveness of cotton gauze with alpha cellulose pads as the collection media to absorb terbufos residues.

**Materials**. Sterilized 12-ply cotton gauze from Abco Inc., Milwaukee, Wisconsin, and alpha-cellulose pads donated by Rayonier Corporation were used as collection media. A thin piece of paper, Kimwipes® from Kimberly-Clark Corporation, Roswell, Georgia, was used to replace glove materials as penetration barriers because Kimwipes® can be penetrated more easily by granular pesticides than glove materials.

**Methods**. The 6x6 cm square paper specimens were backed together with the same size alpha-cellulose pads or cotton gauze by tapes at the edges. A contamination area of 4x4 cm square in

the center of the paper specimen face was marked. Terbufos granules (0.05 g of Counter® 15G) were put evenly on the contamination area of the paper specimens. After one-hour exposure in the covered petri dishes, the granular terbufos was rolled off the specimens. The 6x6 specimens were cut to 4x4 by a scissors and tweezers. Paper specimens were separated from alpha-cellulose pads and discarded to a waste container while alpha-cellulose pads were put into 25 ml of ethyl acetate in test tubes for the 18-hour extraction.

A Varian 3400 gas chromatograph with a thermionic N.P. selective detector was used for analysis of terbufos residues. The operation procedure and parameters of gas chromatography used in this pilot study were the same as those in Experiment 1 of the primary study as described earlier in this chapter.

Each specimen, alpha-cellulose pad or cotton gauze, had three replications. Two GC injections were run per replication. The value of terbufos residue absorbed by the 4x4 cm square collection media was divided by sixteen and converted into the amount of terbufos residue per cm square specimen. The mean and standard deviation of these six values were reported.

**Results and Discussion.** Table 4 presents the amount of terbufos found in alpha-cellulose pads and cotton gauze. A Student's t test (Myers & Well, 1991) was used to determine statistical difference in the mean amount of terbufos absorbed by alpha-cellulose pads and cotton gauze. In all pilot studies,

Table 4. The Amount of Terbufos in Alpha-cellulose Pads and Cotton Gauze

| | Terbufos residue ($\mu g/cm^2$) | |
|---|---|---|
| Materials (n = 6) | Mean | Standard deviation |
| Alpha-cellulose | 1.06 | 0.09 |
| Cotton gauze | 0.50 | 0.12 |

($p < 0.0001$)

statistical significance was set at the 0.05 level of probability.

The t test showed that the amount of terbufos found in alpha-cellulose pads was significantly more than that found in cotton gauze ($p < 0.0001$). This is consistent with earlier Bhat and Perenich (1990) findings reporting that 8-ply gauze as backing material showed a lower level of penetration of pesticides (8.8%) than did alpha-cellulose (12.0%). This difference in the amount of pesticide absorbed by alpha-cellulose and cotton gauze is likely due to the different surface characteristics and structure of the two materials. The surface of alpha-cellulose is smoother and its structure is more compact than that of cotton gauze. Thus, as an absorptive backing material, the smoother alpha-cellulose pads may have more complete contact with the back of the barrier material so that the transfer of pesticide is more efficient. To maximize

possible pesticide transfer and residue collection, alpha-cellulose was selected as backing material to monitor pesticide permeation and penetration through glove materials in the primary study.

**Pilot Study II**

Counter® 15G was used in the previous studies on the contamination and laundering effectiveness of granular terbufos (Stone et al., 1992a; Stone et al., 1993; Stone et al., 1995). In recent years, however, Counter® 15G--granular terbufos--has been replaced by Counter® 20CR in the agricultural pesticide market. Consequently, Counter® 20CR rather than Counter® 15G was used in this study. The purpose of the second pilot study was to compare the contamination levels of glove materials obtained when exposed to a specified weight of Counter® 15G with those obtained from the same weight of Counter® 20CR under the same experimental conditions.

**Materials and Methods**. Barrier laminate (Silver Shield®) gloves obtained from North Safety Products were used for this pilot study. Alpha-cellulose sheets from Rayonier Corporation were used as the collection media. Fifty mg of Counter® 15G and Counter® 20CR granules respectively were used as the contamination amount. Exposure time of glove specimens to terbufos granules was one hour. After exposure, glove specimens were extracted with 25 ml of ethyl acetate for 24 hours.

In this pilot study, the specimen preparation, contamination, and gas chromatography operation procedures and parameters were the same as those in the primary study reported earlier in this chapter. For this pilot study, three replications and two GC injections were made for each pesticide. The terbufos residue in glove specimens was reported as contamination per cm square of glove specimen. These six values were used to compute the mean and standard deviation. A t test was used to determine if the mean amount of terbufos in glove specimens exposed to Counter 15G® and Counter 20CR® were statistically different.

**Results and Discussion.** Table 5 shows the amount of terbufos found in glove specimens exposed to Counter® 15G and Counter® 20CR. The t test result indicated a significant difference between the mean amount of terbufos in glove

Table 5. The Amount of Terbufos in Barrier Laminate Glove Specimens Exposed to Counter® 15G and Counter® 20CR

| | Terbufos residue ($\mu g/cm^2$) | |
|---|---|---|
| Terbufos (n = 6) | Mean | Standard deviation |
| Counter® 15G | 2.36 | 0.20 |
| Counter® 20CR | 0.60 | 0.03 |

($p < 0.0001$)

specimens exposed to Counter® 15G and these exposed to Counter® 20CR ($P < 0.0001$). The amount of terbufos (2.36 $\mu g/cm^2$) in glove specimens exposed to Counter® 15G was about four times higher than that for those (0.6 $\mu g/cm^2$) exposed to Counter® 20CR. One possible explanation is that Counter® 15G may have more contact with the surface of glove specimens than Counter® 20CR because Counter® 15G granules are much smaller than Counter® 20CR granules. Another possible explanation is that the surface of Counter® 15G granules is softer, facilitating the forming of dust, while the surface of Counter® 20CR granules is harder, so less dust forms. This pilot study showed that granular pesticides with same chemical composition but with different physical properties, such as different granule size and hardness, cause different contamination levels in glove materials.

**Pilot Study III**

In most studies on the effectiveness of laundering for decreasing pesticide residues from contaminated fabrics or gloves, pesticide residues were removed from fabrics or gloves with solvent extraction. In theory, the quantity of pesticide residues removed from specimens by means of solvent extraction should be equal to the total quantity of pesticide originally applied to specimens, but in practice the first quantity is less than the second one. The ratio of the two, a percentage of the quantity of pesticide residues removed from specimens by solvent

extraction relative to the total quantity of pesticide originally applied to specimens, is referred to as the pesticide recovery rate. Initial test specimens showed that neoprene glove material might be degraded chemically by ethyl acetate during extraction of tefluthrin residues. The degradation of glove materials disturbed the accurate measurement of pesticide residues by a GC with an electron capture detector due to the presence of an interfering peak generated by degradation components. As a result, ethyl acetate was chosen to extract terbufos residues from glove specimens, but iso-octane was chosen to extract tefluthrin. The purpose of the third pilot study was to compare the pesticide recovery rates of ethyl acetate and iso-octane as extraction solvent after glove materials were exposed to terbufos and tefluthrin.

**Materials and Methods**. Nitrile gloves from Ansell Edmont Industrial Inc. were used for this pilot study. Ten µl of standard terbufos solution (1.43 µg/µl) or ten µl of standard tefluthrin solution (1.0 µg/µl) was used to contaminate glove specimens.

The flat 4x4 cm square specimens were cut from gloves and then were put into petri dishes under a hood. Ten µl of standard solution was dropped on each glove specimen. After 30-minute exposure time, glove specimens were put into 25 ml of ethyl acetate or iso-octane in test tubes for 24-hour extraction. The extracts obtained from the specimens

contaminated by terbufos were concentrated, while the extracts obtained from the specimens contaminated by tefluthrin were diluted to let the their concentration stand within the range of the respective analytical standard.

In the third pilot study, the operational procedures and the parameter of gas chromatograph were the same as those in Experiment 1 of the primary study as described in this chapter. Each glove specimen had three replications. Two GC injections were made per replication. Pesticide recovery rates were expressed as a percentage of the quantity of pesticide residues removed from specimens by solvent extraction relative to the total quantity of pesticide originally applied to specimens. Six values per treatment were used to compute the mean and standard deviation. Two-way analysis of variance was used to determine the effect of pesticide and extraction solvent on pesticide recovery rates. A multiple comparison was conducted among different cells based on a full factorial model with crossed effects and assuming interaction; the mean square error value from this full model was used for estimating the standard error of each difference of means. This multiple comparison further identified the difference in pesticide recovery rates between different treatments.

**Results and Discussion.** Table 6 displays terbufos and tefluthrin recovery rates of ethyl acetate and iso-octane used as extraction solvent for nitrile specimens. The two-way

Table 6. Pesticide Recovery Rates of Ethyl Acetate and Iso-Octane Used as Extraction Solvent for Nitrile Specimens

| | Ethyl acetate | | Iso-octane | |
|---|---|---|---|---|
| Recovery rate % | Mean | SD | Mean | SD |
| Tefluthrin | 91.0 | 5.4 | 89.4 | 5.7 |
| Terbufos | 77.2 | 4.8 | 68.7 | 4.1 |

analysis of variance for terbufos and tefluthrin recovery rates of two different extraction solvents is shown in Table 7.

The results of two-way analysis of variance indicated that there were significant differences in recovery rates between the two different pesticides. The recovery rates of tefluthrin were

Table 7. Two-Way Analysis of Variance for Pesticide Recovery Rates of Ethyl Acetate and Iso-Octane Used as Extraction Solvent

| Source | Degrees of freedom | Sum of squares | Mean square | F value | Pr>F |
|---|---|---|---|---|---|
| Pesticide | 1 | 1783.65 | 1783.65 | 70.4 | 0.0001 |
| Solvent | 1 | 154.53 | 154.53 | 6.10 | 0.0226 |
| Pesticide*Solve | 1 | 72.45 | 72.45 | 2.86 | 0.1063 |
| Error | 20 | 506.70 | 25.33 | | |
| Total | 23 | 2517.34 | | | |

higher than those of terbufos whether ethyl acetate or iso-octane was used as the extraction solvent. Significant differences in pesticide recovery rates also were found between the two extraction solvents. The results of analysis of variance showed that there was no interaction between the pesticide and extraction solvent on the pesticide recovery rates from glove specimens.

Table 8 shows the results of posthoc multiple comparisons among different cell means for pesticide recovery rates of ethyl

Table 8. Multiple Comparisons Among Different Cell Means for Pesticide Recovery Rates of Ethyl Acetate and Iso-Octane Used as Extraction Solvent

| Compared cell means | | | Result |
|---|---|---|---|
| tefluthrin, ethyl acetate | vs. | tefluthrin, iso-octane | ns |
| terbufos, ethyl acetate | vs. | terbufos, iso-octane | ** |
| tefluthrin, ethyl acetate | vs. | terbufos, ethyl acetate | ** |
| tefluthrin, iso-octane | vs. | terbufos, iso-octane | ** |

ns = not significant; ** = significant, $p < 0.05$

acetate and iso-octane used as extraction solvent. The results indicated that there was a significant difference in the recovery rates of terbufos between ethyl acetate and iso-octane used as extraction solvent; however, no differences in the

recovery rates of tefluthrin were found between ethyl acetate and iso-octane used as extraction solvent.

On the one hand, this pilot study provides evidence that iso-octane could replace ethyl acetate as extraction solvent to extract tefluthrin from glove specimens since no significant differences in the recovery rates of tefluthrin were found between ethyl acetate and iso-octane used as extraction solvent. On the other hand, it seems clear that ethyl acetate used for extracting terbufos residues from glove materials was superior to iso-octane since the mean recovery rate of terbufos was higher when ethyl acetate was used as extraction solvent than when iso-octane was used. In light of these results it was decided to use iso-octane for extracting tefluthrin for the primary study.

**Pilot Study IV**

Liquid-liquid extraction, performed in a separatory funnel by solvent, is a traditional method used for extracting pesticide residues in water. This method is tedious and time consuming. In the past years a Semipermeable Polymeric Membrane Device (SPMD) was developed for extracting pesticide residues in water. This method used solvent or lipid materials sealed within a plastic bag for extraction of pesticides in water. Moran (1994) investigated the effectiveness of solvent filled SPMDS in extracting various types of pesticides including organochlorines, organophosphates, pyrethroids, carbamates and

triazines from water. He reported that the solvent-filled SPMDs could effectively extract various types of pesticides in water by methylene chloride in the laboratory tests, but extraction was ineffective for many of organochlorines and pyrethroids.

Water temperature, pesticide properties, and solvents affected the extraction of pesticides by solvent-filled SPMDs (Moran, 1994). Moran found that lower water temperature increased absorption of the pesticides which have high log Kow values, defined as the logarithm of the octanol-water partition coefficient, and low water solubility while higher water temperature raised absorption of the pesticides which have low log Kow values and high water solubility. However, the effect of water temperature on pesticide absorption by a SPMD was effective within a certain range of temperatures. Moran explained that when water temperature was lower, the water solubility decreased for pesticides with a high log Kow value, which made the pesticide more soluble in solvents. Pesticides which have a low log Kow value may shift to being more soluble in solvents with increased temperature.

Solid phase extraction is an effective technique for extraction of the pesticide residues in water by solvent. One recent study (Guo, Stone, & Stahr, 1997) has reported that when a Silica impregnated disk (SIM disk) was used the average recovery rate of disks for extracting terbufos residues from 150 ml water solution was 90 %. However, the recovery rate of tefluthrin from water solution using solid phase extraction was

unknown. The purpose of the fourth pilot study was to determine the recovery rate of tefluthrin from water solution using solid phase extraction techniques.

**Materials and Methods**. Three µl of standard tefluthrin solution (1.0 µg/µl) was dropped into 150 ml of E-Pure® ultra pure water in a beaker. Solid phase extraction techniques were used to extract the tefluthrin residues in 150 ml of water solution by ethyl acetate. The materials used and the solid phase extraction procedure used to extract tefluthrin residues from water were exactly the same as those for solid phase extraction of pesticide residue in the primary study as stated in this chapter.

A Packard 427 gas chromatograph with an electron capture detector was used for the tefluthrin analysis. The parameters of the gas chromatograph used in this pilot study were the same as those used in the primary study in this chapter.

The extracts from water solution were diluted to one-tenth of their original concentration and then were injected into the GC. There were three replicates. Two injections were run for each replicate. The average value of two replicates was used as the amount of tefluthrin from water solution. The recovery rate of tefluthrin from the water solution using solid phase extraction was expressed as a percentage of the amount of tefluthrin extracted from the water solution relative to the amount added originally to the water solution.

**Results and Discussion.** The recovery rates of tefluthrin from 150 ml of water solution using solid phase extraction by ethyl acetate are shown in Table 9. The recovery rates of terbufos by ethyl acetate from a recent study (Guo et al., 1997) also are shown in the same table for comparison. A Student's t test was used to determine statistical difference between tefluthrin and terbufos in the recovery rate from water. The average recovery rate of tefluthrin from water was 76 %. The t test ($p < 0.05$) show this recovery rate was lower than the average recovery rate of terbufos from water solution using the same solid phase extraction techniques.

Table 9. Recovery Rates of Tefluthrin and Terbufos from Water Solution Using Solid Phase Extraction

| | Recovery rate % | |
|---|---|---|
| Pesticide (n = 3) | Mean | Standard deviation |
| Tefluthrin | 76.0 | 2.4 |
| Terbufos | 90.0 | 4.7 |

($p < 0.05$)

# CHAPTER 4. RESULTS AND DISCUSSION

This chapter is presented in two parts: results and discussion. In the first part, due to the complexity of the research design and contamination measurement, the results are discussed separately for terbufos and tefluthrin in each of the three experiments. The effects of exposure time and glove material on the contamination or cleanup of glove materials are presented for each pesticide. Finally the effect of pesticide on the contamination or cleanup of glove materials is discussed. In the second part, the hypotheses proposed in the second chapter are examined based on the results of statistical analyses; then, the findings are discussed.

## Experiment 1: Permeation and Contamination

### Material Permeation

No detectable pesticide contamination was found in any alpha-cellulose pads held under three different glove materials with exposure to granular terbufos or tefluthrin for the six different time periods. Terbufos or tefluthrin did not penetrate glove materials into alpha-cellulose pads within 24 hours of exposure time.

**Terbufos**

The amounts of terbufos residues in the three different glove materials varied with exposure time and glove material. Factorial analysis of variance (ANOVA) was used to determine statistical significance.

**Effect of Exposure Time and Glove Materials.** Six different exposure times (1, 2, 4, 8, 16, and 24 hours) were used in this experiment. As shown in Table 10, the largest mean terbufos contamination of three types of glove materials was in glove specimens with 24 hours exposure (67404 ng/cm$^2$) while the smallest one was in specimens with one hour exposure (3079 ng/cm$^2$). With a longer exposure time, more terbufos residue was

Table 10. Terbufos Residue[a] (ng/cm$^2$) Varies with Exposure Time and Material Type

| | Nitrile | | Neoprene | | Barrier laminate | | |
|---|---|---|---|---|---|---|---|
| Time (Hour) | M | SD | M | SD | M | SD | Mean |
| 1 | 750 | 478 | 5448 | 1227 | 3039 | 250 | 3079 |
| 2 | 916 | 288 | 13753 | 2413 | 5403 | 218 | 6691 |
| 4 | 2182 | 494 | 35229 | 2523 | 9977 | 648 | 15796 |
| 8 | 6729 | 1910 | 49529 | 6071 | 12934 | 878 | 23064 |
| 16 | 16054 | 7497 | 95706 | 9346 | 19624 | 3042 | 43795 |
| 24 | 32360 | 7181 | 134807 | 5897 | 35042 | 2177 | 67404 |

[a] Mean of six values

found in the specimens for all glove materials. Contamination amounts were heaviest in neoprene, followed by barrier laminate and nitrile.

Factorial analysis (Table 11) indicated that the terbufos contamination amount was related significantly to the exposure time, the glove material type and the interaction between these variables ($p < 0.01$) but was not related significantly to the two different observations (Measure).

Table 11. ANOVA for Terbufos Residue in Glove Materials with Different Exposure Times

| Source | Degrees of freedom | Sum of squares ($10^6$) | Mean square ($10^6$) | F value | Pr>F |
|---|---|---|---|---|---|
| Time | 5 | 54710 | 10942 | 658.34 | 0.0001 |
| Glove | 2 | 46116 | 23058 | 1387.32 | 0.0001 |
| Measure | 1 | 20 | 20 | 1.23 | 0.2699 |
| Time*Glove | 10 | 29662 | 2966 | 178.46 | 0.0001 |

Scheffé's test was used to confirm further the difference in contamination levels among glove materials as shown in Table 12. Based on calculations of means using data from all exposure times summed together, the terbufos in neoprene was greatest (55745 ng/cm$^2$), followed by barrier laminate (14336 ng/cm$^2$) and nitrile (9832 ng/cm$^2$).

Table 12. Scheffé Multiple Comparisons Show That Terbufos Residue Varies by Material Type

| Material | Mean ($ng/cm^2$) |
|---|---|
| Nitrile | 9832.19[a] |
| Barrier laminate | 14336.39[b] |
| Neoprene | 55745.21[c] |

Means followed by a different letter are significantly different at $p < 0.05$

**Interaction Effect.** Figure 1 plots the interaction effects of exposure time and material type on terbufos residues in glove materials. The terbufos amounts in nitrile specimens gradually increased with exposure time; after 16 hours, terbufos contamination increased more per hour than before that time. The barrier laminate exhibited slightly higher contamination than the nitrile and increased more sharply before four hours exposure. Compared with nitrile or barrier laminate, the increase of terbufos residues in neoprene was extremely noticeable.

**Linear Regression Between Terbufos Contamination and Exposure Time.** Linear regression (Table 13) was used to identify whether there was a linear relationship between terbufos contamination and exposure time in three glove materials. The neoprene material had the strongest relationship (R-square

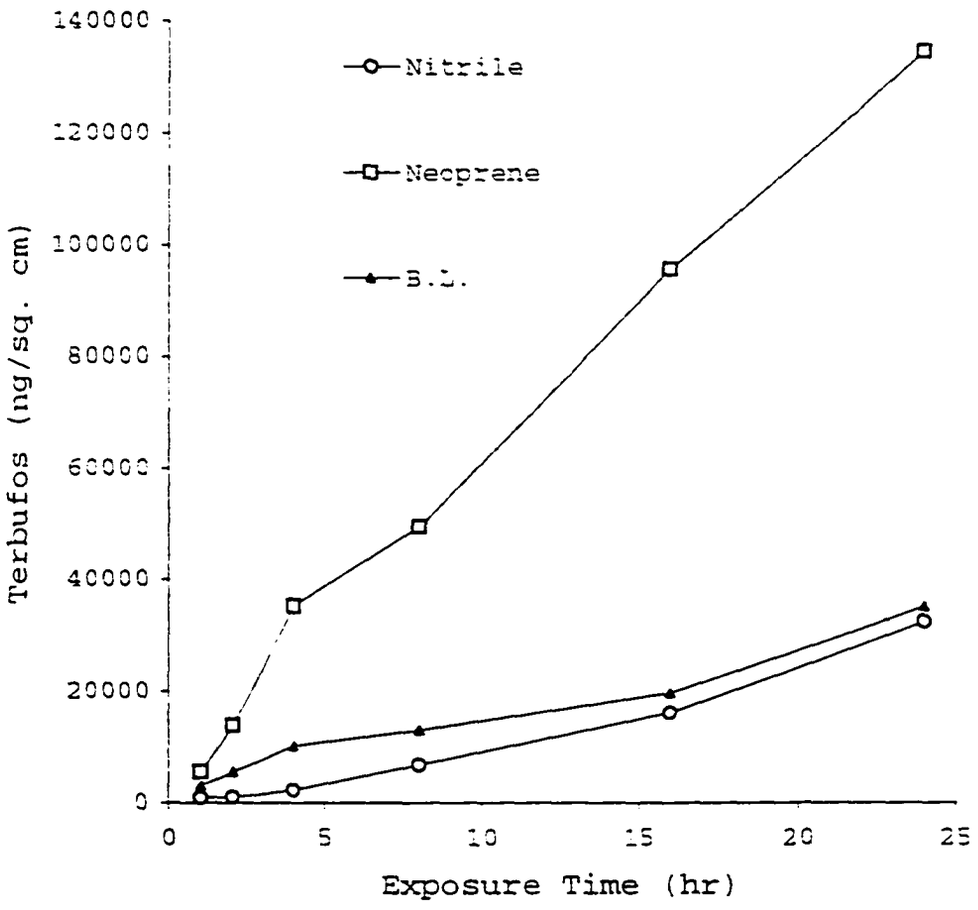



Figure 1. Interaction Effects of Glove Material Type and Exposure Time on Terbufos Residue

Table 13. Regression Results for Terbufos Contamination and Exposure Time

| Material | R square | Pr > F | Intercept ($ng/cm^2$) | Slope |
|---|---|---|---|---|
| Nitrile | 0.8669 | 0.0001 | -2556 | 1351 |
| Neoprene | 0.9801 | 0.0001 | 5324 | 5500 |
| Barrier laminate | 0.9520 | 0.0001 | 2708 | 1269 |

0.98), followed by barrier laminate (R-square 0.95) and nitrile (R-square 0.87).

The results indicated that there were strong linear relationships between terbufos residue and exposure time in each type of glove material ($p < 0.01$). The regressive lines of nitrile, neoprene, and barrier laminate specimens are graphed in Figure 2 and further verify the laboratory observations. Total contamination at the end of the exposure time was much higher for the neoprene than for the barrier laminate and nitrile, which were nearly parallel and very similar in amount. The total contamination for the neoprene at the end of 24 hours was four times greater than that of nitrile.

**Tefluthrin**

The amount of tefluthrin in three different glove material specimens varied with exposure time and material type.

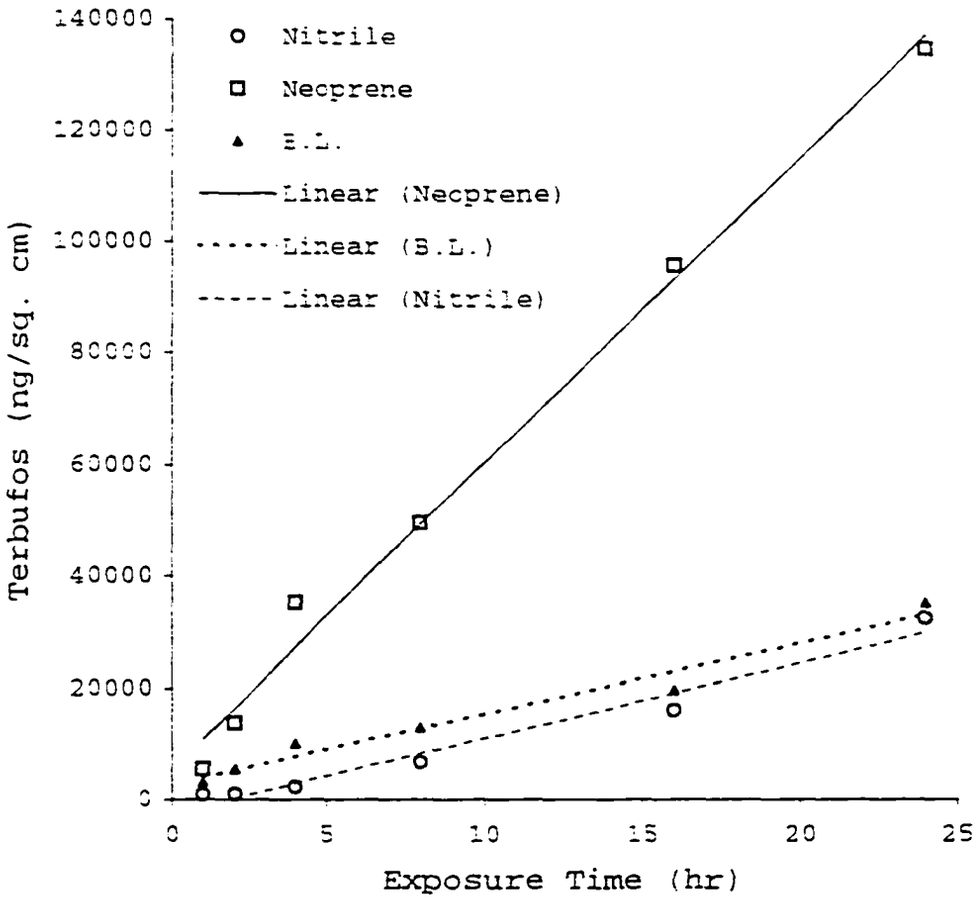



Figure 2. Linear Relationship Between Terbufos Contamination and Exposure Time

Factorial analysis of variance (ANOVA) was used to determine statistical significance.

**Effect of Exposure Time and Glove Materials.** The amounts of tefluthrin residue in glove material specimens varied depending on exposure time. As shown in Table 14, the largest mean tefluthrin contamination of the three types of glove material was in glove specimens with 24 hours exposure (1960 ng/cm$^2$) while the smallest one was in specimens with one hour exposure (233 ng/cm$^2$). The rank order of tefluthrin residues in the three glove material specimens differed from that of terbufos. Tefluthrin contamination amounts were largest in barrier laminate, followed by neoprene and nitrile. As exposure time

Table 14. Tefluthrin Residue[a] (ng/cm$^2$) Varies with Exposure Time and Material Type

| | Nitrile | | Neoprene | | Barrier laminate | | |
|---|---|---|---|---|---|---|---|
| Time (Hour) | M | SD | M | SD | M | SD | Mean |
| 1 | 41 | 16 | 151 | 56 | 698 | 74 | 233 |
| 2 | 35 | 3 | 209 | 48 | 959 | 82 | 401 |
| 4 | 65 | 25 | 186 | 25 | 1503 | 181 | 585 |
| 8 | 66 | 13 | 276 | 104 | 3889 | 296 | 1410 |
| 16 | 50 | 11 | 506 | 222 | 4694 | 210 | 1750 |
| 24 | 48 | 15 | 547 | 51 | 5286 | 234 | 1960 |

[a] Mean of six values of three replications

increased, tefluthrin contamination increased for barrier laminate and neoprene but not for nitrile.

Factorial analysis of variance was used to examine the effects of exposure time and glove material on tefluthrin contamination in glove materials. The results (Table 15) indicated that exposure time, material type, and their interaction had significant effects ($p < 0.01$) on tefluthrin contamination amount in glove materials but different observations (Measure) did not.

Table 15. ANOVA for Tefluthrin Residue in Glove Materials with Different Exposure Times

| Source | Degrees of freedom | Sum of squares | Mean square | F value | Pr>F |
|---|---|---|---|---|---|
| Time | 5 | 40423905 | 8084781 | 457.87 | 0.0001 |
| Glove | 2 | 182617785 | 91308893 | 5171.17 | 0.0001 |
| Measure | 1 | 51791 | 51791 | 2.93 | 0.0905 |
| Glove*Time | 10 | 67956669 | 6795667 | 384.86 | 0.0001 |

Scheffé multiple comparisons (Table 16) further confirm the difference in tefluthrin contamination levels among three types of glove materials. Based on calculations of means using data from all exposure times summed together, the largest mean tefluthrin contamination was in barrier laminate glove specimens (3033 ng/cm$^2$), the second-largest in neoprene specimens (327

Table 16. Scheffé Multiple Comparisons Show That Tefluthrin Residue Varies by Material Type

| Material | Mean ($ng/cm^2$) |
|---|---|
| Nitrile | 50.98[a] |
| Neoprene | 326.99[b] |
| Barrier laminate | 3032.85[c] |

Means followed by a different letter are significantly different at $p < 0.05$

$ng/cm^2$), and the smallest in nitrile specimens (51 $ng/cm^2$). Moreover, mean tefluthrin contamination in barrier laminate specimens was far larger than that in neoprene specimens or in nitrile specimens.

**Interaction Effect**. The interaction of exposure time and material type is graphed in Figure 3. The tefluthrin residues in nitrile specimens were almost constant as exposure time increased from 1 hour to 24 hours. The contamination in neoprene slowly increased until 16 hours and then basically remained constant. Compared with the other two types of glove materials, tefluthrin residues in barrier laminate specimens increased sharply as exposure time increased.

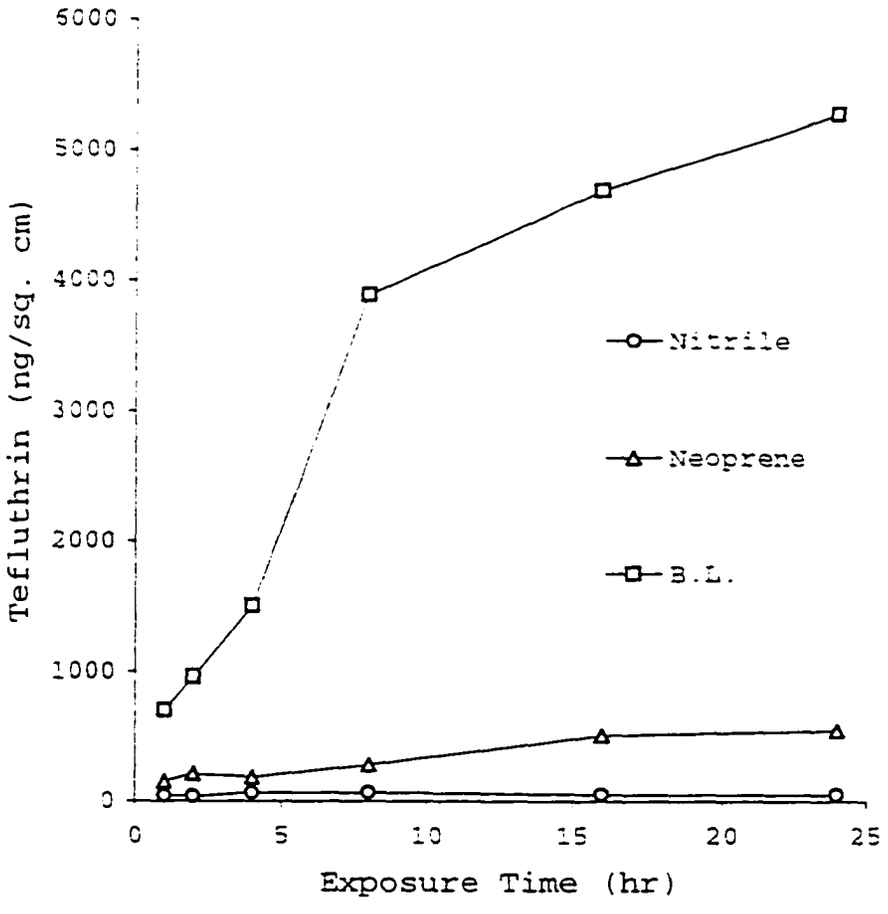



Figure 3. Interaction Effects of Glove Material Type and Exposure Time on Tefluthrin Residue

**Linear Regression Between Tefluthrin Contamination and Exposure Time**. Linear regression (Table 17) was used to identify whether there was a linear relationship between tefluthrin contamination and exposure time in three glove materials. The results indicated that the barrier material had the highest relationship (R-square 0.85), followed by neoprene (R-square 0.66), and nitrile material (R-square 0.0052).

Table 17. Regression Results for Tefluthrin Contamination and Exposure Time

| Material | R square | Pr > F | Intercept ($ng/cm^2$) | Slope |
|---|---|---|---|---|
| Nitrile | 0.0052 | 0.6750 | 50 | 0.16 |
| Neoprene | 0.6597 | 0.0001 | 147 | 18.14 |
| Barrier laminate | 0.8482 | 0.0001 | 1030 | 202.09 |

The results indicated that there were strong linear relationships between tefluthrin residue and exposure in barrier laminate and neoprene materials ($p < 0.01$). There was no linear relationship between tefluthrin residue and exposure in nitrile material. The regression lines of nitrile, neoprene, and barrier laminate specimens are graphed in Figure 4. The tefluthrin contamination in nitrile hardly varied with increased exposure time.

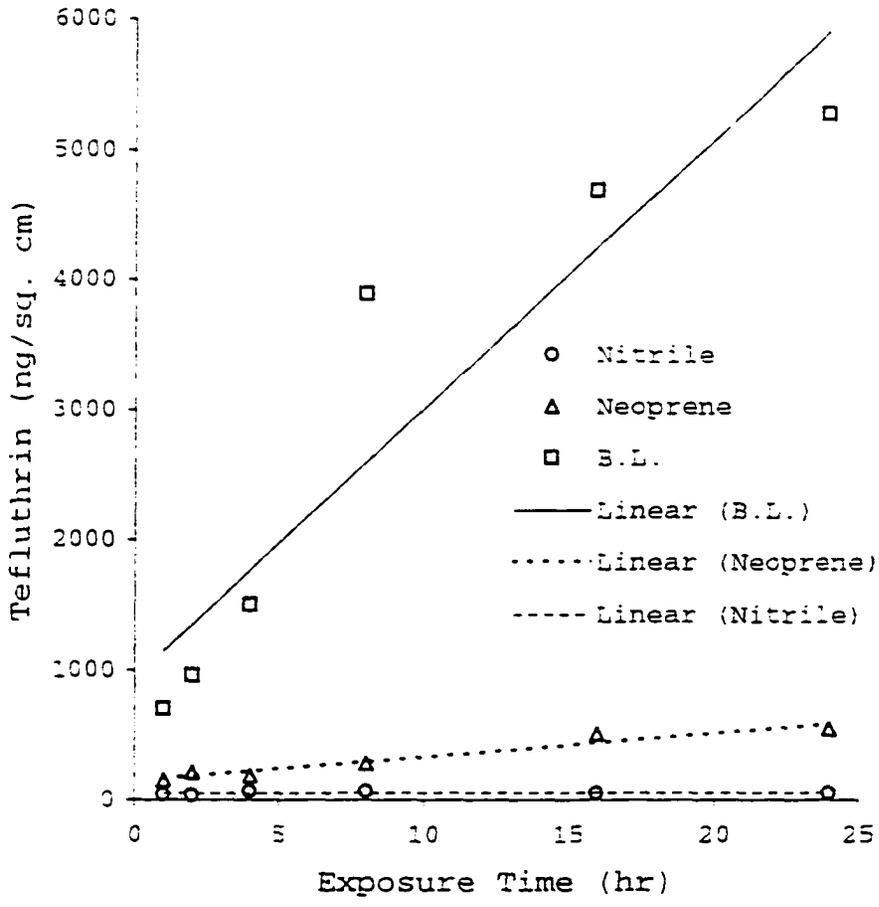



Figure 4. Linear Relationship Between Tefluthrin Contamination and Exposure Time

**Pesticide Effect**

Table 18 shows the results of factorial analysis of variance with pesticide included as a variable in addition to exposure time and glove material type. The results indicated contamination in glove materials differed significantly by pesticide ($p < 0.01$). The terbufos residue in a glove specimen under a certain experimental treatment was much higher than the tefluthrin residue in the same experimental treatment.

The statistical examination of the experimental data confirmed that the differences in contamination levels in glove materials observed in the laboratory were related significantly to exposure time, glove material type, and pesticide type.

Table 18. ANOVA Shows That Material Contamination Differs Significantly by Pesticide

| Source | Degrees of freedom | Sum of squares ($10^6$) | Mean square ($10^6$) | F value | Pr>F |
|---|---|---|---|---|---|
| Pesticide | 1 | 34198 | 34198 | 392.55 | 0.0001 |
| Time | 5 | 29094 | 5819 | 66.79 | 0.0001 |
| Glove | 2 | 22973 | 11486 | 131.85 | 0.0001 |
| Measure | 1 | 50 | 50 | 0.57 | 0.4505 |
| Pesticide*time | 5 | 24864 | 4973 | 57.08 | 0.0001 |
| Pesticide*glove | 2 | 24078 | 12039 | 138.19 | 0.0001 |
| Time*glove | 10 | 15279 | 1528 | 17.54 | 0.0001 |

## Experiment 2: Effects of Cleanup Methods on Reduction of Pesticide Contamination

### Terbufos

The terbufos residues in three different glove material specimens before and after laundering are shown in Table 19. After flush or Launder-Ometer wash (hereafter referred to as LOM), the largest terbufos residue was found in neoprene glove

Table 19. Terbufos Residue (ng/cm$^2$) in Glove Materials Before and After Cleanup

| | Nitrile | Neoprene | Barrier laminate |
|---|---|---|---|
| 3 minutes | | | |
| Control* | 79.79[a] | 314.17[a] | 348.23[a] |
| Flush | 27.19[b] | 120.73[b] | 244.90[b] |
| Launder-Ometer | 30.10[b] | 313.54[a] | 178.75[b] |
| 30 minutes | | | |
| Control* | 431.25[a] | 2000.20[a] | 1141.88[a] |
| Flush | 496.04[a] | 1890.90[a] | 1141.35[a] |
| Launder-Ometer | 140.42[b] | 1864.80[a] | 727.81[b] |

Means followed by a different letter within the same glove material and time treatments are significantly different at $p < 0.05$

* Before laundering

specimens with 30-minute exposure (1890.90 ng/cm$^2$), while the smallest terbufos residue was in the nitrile with 3-minute exposure (27.19 ng/cm$^2$).

Both flush and LOM cleanup methods reduced terbufos residues in nitrile and barrier laminate specimens as compared to the control with 3-minute exposure time. After the flush treatment, terbufos residues were 66% lower for nitrile and 30% lower for barrier laminate. However, there was no significant difference between flush and LOM in the reduction of terbufos residues from nitrile and barrier laminate specimens. Flush significantly reduced terbufos residue in neoprene specimens. After flush, terbufos residues were 62% lower for neoprene, but LOM did not reduce significantly terbufos residues in neoprene specimens.

After the 30-minute exposure time, LOM reduced terbufos residues in nitrile and barrier laminate specimens significantly. After LOM, terbufos residues were 67% lower for nitrile and 36% lower for barrier laminate. However, flush did not remove terbufos residues significantly. Neither flush nor LOM effectively reduced terbufos residue in the neoprene glove material.

Factorial analysis of variance was used to determine which variables in the experimental design were related significantly to contamination levels with different cleanup methods. Scheffé multiple comparisons were used to identify further the differences among the different levels in the variable.

**Glove Material, Exposure Time, and Cleanup Effects.** A significant difference ($p < 0.01$) in terbufos residue retention was found among the types of glove materials, as shown in Table 20. The terbufos residue in the neoprene glove materials was higher than in barrier laminate and nitrile after cleanup treatments, as Scheffé results show (Table 21). The least contamination after cleanup was found in the nitrile specimens, whether the exposure time was 3 or 30 minutes (Table 19). The rank order of the three glove materials in terbufos residue retention was consistent with that of the three glove materials in contamination levels.

Table 20. ANOVA for Terbufos Residue in Glove Materials with Different Cleanup Methods

| Source | Degrees of freedom | Sum of squares | Mean square | F value | Pr>F |
|---|---|---|---|---|---|
| Glove | 2 | 14046216 | 7023108 | 178.49 | 0.0001 |
| Method | 2 | 574183 | 287091 | 7.30 | 0.0012 |
| Time | 1 | 22289366 | 22289366 | 566.47 | 0.0001 |
| Measure | 1 | 43953 | 43953 | 1.12 | 0.2934 |
| Glove*method | 4 | 385648 | 96412 | 2.45 | 0.0518 |
| Glove*time | 2 | 8665620 | 4332810 | 110.12 | 0.0001 |
| Method*time | 2 | 444374 | 222187 | 5.65 | 0.0049 |
| Error | 89 | 3501951 | 39348 | | |
| Total | 107 | 49971693 | | | |

Table 21. Scheffé Multiple Comparisons Show That Terbufos Residue Varies by Glove Materials, Exposure Time, and Cleanup Methods

| Main effect | Level | Statistical grouping | Mean ($ng/cm^2$) |
|---|---|---|---|
| Glove | Nitrile | a | 200.80 |
| | Barrier laminate | b | 630.49 |
| | Neoprene | c | 1084.06 |
| Time | 3 minutes | a | 184.16 |
| | 30 minutes | b | 1092.74 |
| Method | Control | a | 719.25 |
| | Flush | ab | 653.52 |
| | Launder-Ometer | b | 542.57 |

Means with different letters are significantly different at $p < 0.05$

A significant difference ($p < 0.01$) in terbufos residue retention also was found between 3-minute and 30-minute exposure time, as Table 20 shows. For all materials, contamination levels were higher with 30-minute exposure (Table 21) and cleanup was less effective (Table 19). The factorial analysis of variance also showed that the cleanup method was a significant variable in explaining terbufos retention ($p < 0.01$). For all materials, the LOM was more effective than the

flush in the reduction of terbufos residue as the Scheffé's test shows (Table 21). However, as clearly shown by the data in Table 19, the effectiveness of the cleanup was both time-and material-dependent.

**Interaction Effect.** The factorial analysis of variance also identified significant interactions among all primary variables: glove material and cleanup method; glove material and exposure time; and cleanup method and exposure time. After 30-minute exposure and LOM, neoprene performed worse than nitrile and barrier laminate in retaining terbufos contamination, but after 3-minute exposure with the flush method, the percent reduction in contamination for neoprene was almost the same for the other materials.

**Tefluthrin**

Table 22 shows the tefluthrin residues in three different glove materials before and after different cleanup treatments. After flush or LOM, tefluthrin residues in glove materials ranged from 27.19 to 1890.90 ng/cm$^2$, with the smallest tefluthrin residues in nitrile for the 3-minute exposure and the largest tefluthrin residues in neoprene glove materials for the 30-minute exposure.

Both flush and LOM reduced tefluthrin residues significantly for each type of glove material with the 3-minute exposure time. Compared with flush treatment for terbufos,

Table 22. Tefluthrin Residue (ng/cm$^2$) in Glove Materials Before and After Cleanup

| | Nitrile | Neoprene | Barrier laminate |
|---|---|---|---|
| 3 minutes | | | |
| Control* | 57.31[a] | 89.98[a] | 242.45[a] |
| Flush | 4.05[b] | 19.75[b] | 142.19[b] |
| Launder-Ometer | 0.18[b] | 6.46[b] | 53.33[c] |
| 30 minutes | | | |
| Control* | 63.82[a] | 149.39[a] | 553.65[a] |
| Flush | 7.90[b] | 136.73[a] | 488.28[ab] |
| Launder-Ometer | 0.15[b] | 18.91[b] | 270.97[b] |

Means followed by a different letter within the same glove material and time treatments are significantly different at $p < 0.05$

*Before laundering

tefluthrin residue could be removed more effectively from glove materials by flush. After flush, tefluthrin residues were 93% lower for nitrile, 78% lower for neoprene, and 41% lower for barrier laminate. However, no significant differences were found between flush and LOM for nitrile and neoprene. LOM was significantly more effective than flush for barrier laminate. After LOM, tefluthrin residues were 78% lower for barrier laminate.

After the 30-minute exposure time, LOM reduced tefluthrin residues significantly for neoprene and barrier laminate, but flush did not remove tefluthrin residues significantly; after LOM, tefluthrin residues were 87% lower for neoprene and 51% lower for barrier laminate. Either flush or LOM effectively reduced tefluthrin residues from nitrile, but no significant differences were found between the two cleanup methods for nitrile. After LOM, most tefluthrin residues were removed from the nitrile materials.

The factorial analysis of variance was used to determine whether glove material, exposure time, and cleanup method affected the reduction of tefluthrin residues. Scheffé's test was used to identify further the differences among the levels in these variables.

**Glove Material, Exposure Time, and Cleanup Effects**. A significant difference ($p < 0.01$) in tefluthrin residue retention was observed among different glove materials, as shown in Table 23. The tefluthrin residue retention in barrier laminate materials was much higher than that in neoprene and nitrile; the smallest tefluthrin retention was in nitrile materials, as Scheffé's test shows (Table 24). The rank order of three glove materials in tefluthrin residue retention after laundering accorded with that of the three glove materials in contamination levels.

ANOVA indicated that there was a significant difference (p

Table 23. ANOVA for Tefluthrin Residue in Glove Materials with Different Cleanup Methods

| Source | Degrees of freedom | Sum of squares | Mean square | F value | Pr>F |
|---|---|---|---|---|---|
| Glove | 2 | 1488991 | 744495 | 147.58 | 0.0001 |
| Method | 2 | 326688 | 163344 | 32.38 | 0.0001 |
| Time | 1 | 384552 | 384552 | 76.23 | 0.0001 |
| Measure | 1 | 6168 | 6168 | 1.22 | 0.2718 |
| Glove*method | 4 | 113578 | 28394 | 5.63 | 0.0004 |
| Glove*time | 2 | 416710 | 208355 | 41.30 | 0.0001 |
| Method*time | 2 | 28599 | 14299 | 2.83 | 0.0641 |
| Error | 89 | 448964 | 5045 | | |
| Total | 107 | 3228634 | | | |

< 0.01) in tefluthrin residue retention between 3-minute exposure and 30-minute exposure, as shown in Table 23. For all materials, after cleanup the tefluthrin contamination with 3-minute exposure was much lower than that with 30-minute exposure, as shown in Table 24. Factorial analysis of variance also showed a significant difference ($p < 0.01$) in tefluthrin retention between different cleanup methods. Considering all data, the LOM was more effective than the flush in the reduction of tefluthrin residue, as the Scheffé test shows (Table 24). However, as clearly shown by the results summarized in Table 22,

Table 24. Scheffé Multiple Comparisons Show That Tefluthrin Residue Varies by Glove Material, Exposure Time, and Cleanup Methods

| Main effect | Level | Statistical grouping | Mean ($ng/cm^2$) |
|---|---|---|---|
| Glove | Nitrile | a | 22.24 |
| | Neoprene | b | 70.20 |
| | Barrier laminate | c | 291.81 |
| Time | 3 minutes | a | 68.41 |
| | 30 minutes | b | 187.75 |
| Method | Control | a | 192.77 |
| | Flush | b | 133.15 |
| | Launder-Ometer | c | 58.33 |

Means with different letters are significantly different at $p < 0.05$

the effectiveness of the cleanup was both time-and material-dependent.

**Interaction Effect.** The factorial analysis of variance identified two significant interactions among variables: glove material and cleanup method; and glove material and exposure time. With nitrile material, either flush or wash could reduce tefluthrin residues effectively, but with neoprene and barrier

laminate, LOM was much better than flush in reducing tefluthrin contamination from materials, especially with the 30-minute exposure times. There was a trend toward a possible interaction between cleanup method and exposure time ($p < 0.065$), although not statistically significant at the 0.05 probability level. With the 3-minute exposure time, flush reduced tefluthrin residues significantly for each type of glove material. However, after the 30-minute exposure time, flush could not remove tefluthrin residues significantly for neoprene and barrier laminate.

**Pesticide Effect**

ANOVA was used to examine the results of GC analysis for the whole laundering data set, including both terbufos and tefluthrin ($n = 216$). Table 25 shows the results. ANOVA indicated that the amount of pesticide residue found in glove materials after laundering differed significantly ($p < 0.001$) by pesticide type, glove material type, cleanup method, and exposure time. Interaction effects between variables were significant ($p < 0.001$) for pesticide and glove material, pesticide and exposure time, and glove material and exposure time. The interaction effect between cleanup method and exposure time also was significant at the $p < 0.05$ level. No significant difference was found for interaction effects between pesticide and cleanup method or between glove material and cleanup method. After laundering, the terbufos residue found in

Table 25. ANOVA for Residue in Glove Materials with Different Pesticides, Cleanup Methods, and Exposure Times

| Source | Degrees of freedom | Sum of squares ($10^6$) | Mean square ($10^6$) | F value | Pr>F |
|---|---|---|---|---|---|
| Pesticide | 1 | 14065603 | 14065603 | 310.33 | 0.0001 |
| Glove | 2 | 8459804 | 4229902 | 93.32 | 0.0001 |
| Method | 2 | 882100 | 441050 | 9.73 | 0.0001 |
| Time | 1 | 14264657 | 14264657 | 314.72 | 0.0001 |
| Measure | 1 | 41525 | 41525 | 0.92 | 0.3397 |
| Pesti*glove | 2 | 7075402 | 3537701 | 78.05 | 0.0001 |
| Pesti.*method | 2 | 18771 | 9385 | 0.21 | 0.8131 |
| Pesti*time | 1 | 8409261 | 8409261 | 185.53 | 0.0001 |
| Glove*method | 4 | 333579 | 83395 | 1.84 | 0.1227 |
| Glove*time | 2 | 4527765 | 2263882 | 49.95 | 0.0001 |
| Method*time | 2 | 349041 | 174521 | 3.85 | 0.0229 |
| Error | 195 | 8838421 | 45325 | | |
| Total | 215 | 67265930 | | | |

glove materials was much higher than the tefluthrin residue under the same treatment conditions, as shown in Table 19 and Table 22.

**Pesticides in Laundering Solution**

The amounts of pesticide found in laundering solution used for laundering glove specimens with different cleanup methods and exposure times are shown in Table 26. The amount of pesticide found in laundering solution varied with pesticide type, glove material, cleanup method, and exposure time.

With the three-minute exposure, the amount of terbufos found in the flush solution ranged from 0.6 ng/ml for barrier

Table 26. Pesticide Found in Laundering Solution Used for Different Cleanup Methods (ng/150 ml)

| | Terbufos | | | Tefluthrin | | |
|---|---|---|---|---|---|---|
| | Nitrile | Neoprene | B.L. | Nitrile | Neoprene | B.L. |
| 3 mins. | | | | | | |
| Flush | 232 | 283 | 90 | 181 | 107 | 114 |
| ng/ml | 1.5 | 1.9 | 0.6 | 1.2 | 0.7 | 0.8 |
| Wash | 257 | 123 | 102 | 116 | 187 | 262 |
| ng/ml | 1.7 | 0.8 | 0.7 | 0.8 | 1.2 | 1.7 |
| 30 mins. | | | | | | |
| Flush | 185 | 353 | 175 | 142 | 159 | 119 |
| ng/ml | 1.2 | 2.4 | 1.2 | 0.9 | 1.1 | 0.8 |
| Wash | 485 | 322 | 2706 | 78 | 135 | 218 |
| ng/ml | 3.2 | 2.1 | 18.0 | 0.5 | 0.9 | 1.5 |

laminate to 1.9 ng/ml for neoprene; the amount of tefluthrin ranged from 0.7 ng/ml for neoprene to 1.2 ng/ml for nitrile. With 30-minute exposure, the flush solution contained terbufos in amounts ranging from 1.2 ng/ml in barrier laminate and nitrile to 2.4 ng/ml for neoprene, whereas with tefluthrin, the amounts ranged from 0.8 ng/ml for barrier laminate to 1.1 ng/ml for neoprene. Data in Table 26 suggests that the amounts of pesticide contained in LOM wash solution were more variable.

To determine the effects of pesticide type, glove material, cleanup method, and exposure time on the amount of pesticide in laundering solution, ANOVA including the entire data set for both pesticides ($n = 144$) were used. The results of this test are shown in Table 27.

There was a significant difference in solution contamination ($p < 0.01$) between the pesticides, terbufos and tefluthrin. The mean amount of terbufos found in the solution was higher than that of tefluthrin.

Significant differences in solution contamination were found among the three glove materials ($p < 0.05$) and between the two cleanup methods ($p < 0.01$). More pesticide was found in the LOM solution than in the flush solution.

A significant difference in solution contamination also was found between the 3- and 30-minute exposure time. The mean amount of pesticide in the solution from the 3-minute exposure was smaller than that from 30-minute exposure.

ANOVA also identified several significant interaction

Table 27. ANOVA for Pesticide in Laundering Solutions from Two Cleanup Methods

| Source | Degrees of freedom | Sum of squares | Mean square | F value | Pr>F |
|---|---|---|---|---|---|
| Pesticide | 1 | 3052591 | 3052591 | 10.73 | 0.0014 |
| Glove | 2 | 2231340 | 1115670 | 3.92 | 0.0222 |
| Method | 1 | 2031575 | 2031575 | 7.14 | 0.0085 |
| Time | 1 | 2286144 | 2286144 | 8.04 | 0.0053 |
| Measure | 1 | 5353 | 5353 | 0.02 | 0.8911 |
| Pesti*glove | 2 | 1613659 | 806829 | 2.84 | 0.0623 |
| Pesti.*method | 1 | 1566252 | 1566252 | 5.51 | 0.0205 |
| Pesti*time | 1 | 2647671 | 2647671 | 9.31 | 0.0028 |
| Glove*method | 2 | 3847586 | 1923793 | 6.77 | 0.0016 |
| Glove*time | 2 | 3047007 | 1523504 | 6.36 | 0.0058 |
| Method*time | 1 | 1917302 | 1917302 | 6.74 | 0.0105 |
| Error | 128 | 36398848 | 284366 | | |
| Total | 143 | 60645329 | | | |

effects ($p < 0.05$) in these data. Interactions were significant between pesticide and cleanup method, pesticide and exposure time, glove material and cleanup method, glove material and exposure time, and cleanup method and exposure time.

## Experiment 3: Effects of Laundering Parameters on Reduction of Pesticide Contamination

### Terbufos

The terbufos residues in three glove materials after different laundering treatments are shown in Table 28. After the cleanup treatments, the amount of terbufos residues in glove materials ranged from 140.4 ng/cm$^2$ for nitrile washed in hot water and detergent to 1864.8 ng/cm$^2$ for neoprene with the same treatment.

To determine the effectiveness of each cleanup method on the reduction of terbufos residues for each type of glove material, the amount of terbufos found in laundered specimens was compared with contaminated control specimens. These comparisons also are shown in Table 28. High-temperature

Table 28. Effects of Laundering Temperature and Detergent on Terbufos Retention in Three Glove Materials (ng/cm$^2$)

| | | Detergent | | No detergent | |
|---|---|---|---|---|---|
| Material | Control | High tem. | Low tem. | High tem. | Low tem. |
| Nitrile | 431.25 | 140.42* | 144.17* | 442.81 | 462.40 |
| Neoprene | 1999.80 | 1864.80 | 1331.50* | 1486.00* | 1859.40 |
| B. L. | 1141.88 | 727.81* | 468.13* | 722.19* | 825.42* |

Means followed by * are significantly different from the control mean of the same glove materials at $p < 0.05$

laundering ($60^0$C) with detergent reduced terbufos residue 67% for nitrile, 36% for barrier laminate, and not at all for neoprene. Cleanup results were much worse when no detergent was used.

ANOVA was used again to determine the significant variables in the experimental design. The main effects of glove material, temperature, and detergent on reduction of terbufos residues are shown in Table 29.

Table 29. ANOVA for Effect of Glove Material, Temperature, and Detergent on Terbufos Residue After LOM Wash

| Source | Degrees of freedom | Sum of squares ($10^6$) | Mean square ($10^6$) | F value | Pr>F |
|---|---|---|---|---|---|
| Glove | 2 | 22741229 | 11370615 | 348.02 | 0.0001 |
| Temperature | 1 | 42961 | 42961 | 1.31 | 0.2561 |
| Detergent | 1 | 628834 | 628834 | 19.25 | 0.0001 |
| Measure | 1 | 4552 | 4552 | 0.14 | 0.7103 |
| Glove*temp. | 2 | 32974 | 16487 | 0.50 | 0.6063 |
| Glove*deter. | 2 | 167809 | 83904 | 2.57 | 0.0852 |
| Temp.*deter. | 1 | 826148 | 826148 | 25.29 | 0.0001 |
| Error | 59 | 1927655 | 32672 | | |
| Total | 71 | 26977021 | | | |

**Glove Material Effect**. There were significant differences ($p < 0.01$) among the types of glove materials in terbufos residue retention. The results of GC analysis showed that the largest terbufos residue retention was in neoprene glove specimens, the second-largest in barrier laminate, and the smallest in nitrile. The rank order of the three glove materials in terbufos residue retention also was consistent with that of Experiment 1 and Experiment 2. Scheffé multiple comparisons (Table 30) indicated that the mean terbufos amounts differed significantly among the three types of glove materials.

**Laundering Parameter Effect**. The effect of temperature on terbufos retention in glove materials after LOM wash was not significant. However, a significant difference ($p < 0.01$) in terbufos residue was found between usage of detergent and its absence. The results indicated that the mean residue was lower in specimens washed with detergent than those without detergent.

Multiple comparisons among the combination of different laundering parameters and the control value for each glove material were computed to determine the effect of detergent and temperature on terbufos retention in each type of glove material. The results are shown in Table 31.

With all three glove materials, the terbufos residue varied significantly between the control specimens and the specimens washed with detergent ($p < 0.01$). For neoprene and barrier laminate a significant difference was found between the control

Table 30. Scheffé Multiple Comparisons Show That Terbufos Residue Varied with Glove Material and Detergent Use

| Main effect | Level | Statistical grouping | Mean ($ng/cm^2$) |
|---|---|---|---|
| Glove | Nitrile | a | 297.45 |
| | Neoprene | b | 1635.42 |
| | Barrier laminate | c | 685.89 |
| Temperature | High | a | 897.34 |
| | Low | a | 848.49 |
| Detergent | Yes | a | 779.46 |
| | No | b | 966.37 |

Means with a different letter are significantly different at $p < 0.05$

specimens and those washed with no detergent (just water), but no significant difference was found between the control and the no detergent wash for neoprene. Comparing the detergent versus no detergent wash specimens, a significant difference was found for nitrile and barrier laminate materials, but not for neoprene.

With nitrile glove materials, neither high- nor low-temperature wash differed significantly from the control in terbufos residue. A higher wash temperature offers no

Table 31. Comparison Among Different Laundering Parameters and Control in Terbufos Residues for Each Glove Material

| | Glove material | | |
|---|---|---|---|
| Contrast group | Nitrile | Neoprene | B. L. |
| Detergent vs. control | ** | ** | ** |
| No detergent vs. control | ns | * | ** |
| Detergent vs. no detergent | ** | ns | ** |
| High temp. vs. control | ns | * | ** |
| Low temp. vs. control | ns | ** | ** |
| High temp. vs. low temp. | ns | ns | * |

** = Comparison was significant at $p < 0.01$

* = Comparison was significant at $p < 0.05$

ns = Not significant

beneficial effect for nitrile.

With the neoprene, each laundering treatment differed significantly from the controls ($p < 0.05$), but the treatments themselves were not significantly different from each other. That is, it made no difference if high- or low-temperature wash were used nor if detergent or no detergent were used in the wash process, but washing one way or another helped reduce residue as compared to the control.

With the barrier laminate material, there were significant differences in all comparisons of variables tested. However, this result must be considered in relation to findings shown in Table 28: Terbufos residues were lower when detergent was used than when it was not. After laundering with detergent, terbufos residues were 48% lower when detergent was used, but only 32% lower when no detergent was used. Also, terbufos residues were 43% lower when low-temperature wash was used, compared to 37% lower with high-temperature wash.

**Interaction Effect.** Table 31 showed a significant interaction effect ($P < 0.01$) between temperature and detergent variables. With the low wash temperature, detergent significantly reduced terbufos residues, especially in barrier laminate glove specimens.

**Tefluthrin**

Table 32 gives the amount of tefluthrin residue in three glove materials after treatments with different laundering parameters. After different laundering treatments the amount of tefluthrin in the material ranged from no detectable amount for neoprene in the low-temperature wash with detergent to 270.97 $ng/cm^2$ for the barrier laminate with high-temperature wash and detergent. Like the statistical analysis for terbufos, the amount of tefluthrin in a glove specimen was compared with the control specimen within the same glove material type to

Table 32. Effects of Laundering Temperature and Detergent on Tefluthrin Retention in Three Glove Materials ($ng/cm^2$)

| Material | Control | Detergent | | No detergent | |
|---|---|---|---|---|---|
| | | High tem. | Low tem. | High tem. | Low tem. |
| Nitrile | 63.82 | 0.15* | 0.39* | 0.21* | 1.08* |
| Neoprene | 147.82 | 18.91* | nda[a]* | 13.66* | 15.08* |
| B. L. | 657.81 | 270.97* | 172.03* | 235.10* | 257.27* |

Means followed by * are significantly different from the control mean of the same glove materials at $p < 0.05$ level

[a] No detectable amount

determine the effect of each treatment on the reduction of tefluthrin residue for each type of glove material. The results of statistical analyses are reported in Table 32.

Factorial analysis of variance was used to determine the effects of glove material, laundering temperature, and detergent on reduction of tefluthrin residues. The results are shown in Table 33.

**Glove Material Effect**. A significant difference ($p < 0.01$) was found among the types of glove materials in tefluthrin residue retention. Sheffé multiple comparisons (Table 34) showed that the largest tefluthrin residue was in barrier laminate specimens, followed by neoprene and nitrile.

Table 33. ANOVA Shows Effects of Temperature and Detergent on Tefluthrin Residue in Glove Materials

| Source | Degrees of freedom | Sum of squares | Mean square | F value | Pr>F |
|---|---|---|---|---|---|
| Glove | 2 | 83083605 | 415418.03 | 3224.33 | 0.0001 |
| Temperature | 1 | 4337.59 | 4337.59 | 34.67 | 0.0001 |
| Detergent | 1 | 1798.19 | 1798.19 | 13.96 | 0.0004 |
| Measure | 1 | 49.10 | 49.10 | 0.38 | 0.5394 |
| Glove*temp. | 2 | 4963.18 | 2481.59 | 19.26 | 0.0001 |
| Glove*deter. | 2 | 2005.56 | 1002.28 | 7.78 | 0.0001 |
| Temp.*deter. | 1 | 10092.21 | 10092.21 | 78.33 | 0.0001 |
| Error | 59 | 7601.47 | 128.84 | | |
| Total | 71 | 874210.23 | | | |

**Laundering Parameter Effect.** The effect of laundering parameters on tefluthrin retention in glove materials was significant (Table 34). A significant difference ($p < 0.01$) was found between usage of detergent and its absence. Tefluthrin residues on glove materials washed with detergent was lower when no detergent was used. Based on mean values (Table 34), the effect of laundering temperature on tefluthrin retention in glove materials also was significant ($p < 0.01$) with less residue found when materials were washed at the lower temperature.

Table 34. Scheffé Multiple Comparisons Show That Tefluthrin Residue Varied with Glove Material, Laundering Temperature, and Detergent

| Main effect | Level | Statistical grouping | Mean(ng/cm$^2$) |
|---|---|---|---|
| Glove | Nitrile | a | 0.457 |
| | Neoprene | b | 11.911 |
| | Barrier laminate | c | 233.844 |
| Temperature | High | a | 89.832 |
| | Low | b | 74.309 |
| Detergent | Yes | a | 77.073 |
| | No | b | 87.068 |

Means with different letters are significantly different at $p < 0.05$

To determine further the effect of laundering parameters on tefluthrin retention in each type of glove material, multiple comparisons were conducted among the combinations of different laundering parameters and control values for each glove material, as shown in Table 35.

With all glove materials, significant differences were found in tefluthrin residues between each laundering treatment (high temperature, low temperature, detergent and no-detergent) and their respective controls. After each laundering treatment,

Table 35. Comparison Among Different Laundering Parameters and Control in Tefluthrin Residues for Each Glove Material

| | Glove material | | |
|---|---|---|---|
| Contrast group | Nitrile | Neoprene | B. L. |
| Detergent vs. control | ** | ** | ** |
| No detergent vs. control | ** | ** | ** |
| Detergent vs. no detergent | ns | ns | * |
| High temp. vs. control | ** | ** | ** |
| Low temp. vs. control | ** | ** | ** |
| High temp. vs. low temp. | ns | ns | ** |

** = Comparison was significant at $p < 0.01$ level

* = Comparison was at $p < 0.07$ level

ns = Not significant

98% of tefluthrin residue was removed from nitrile and 90% was removed from neoprene (Table 32). However, no significant differences in tefluthrin retention were found between high temperature and low temperature or between detergent and no-detergent for nitrile and neoprene. With barrier laminate significant differences in tefluthrin residues ($p < 0.01$) were found between high and low temperature. After laundering with low temperature, tefluthrin residues in barrier laminate were 67% lower, but with high temperature they were 62% lower (Table

32). Tefluthrin residues appeared to be less when detergent was used than when not, but this relationship was only at the $p < 0.07$ level. After laundering with detergent, tefluthrin residues were 66% lower; with no-detergent, they were 63% lower (Table 32).

**Interaction Effect**. Several significant ($P < 0.01$) interactions were found (Table 35) between glove material and temperature, between glove material and detergent, and between temperature and detergent. With nitrile or neoprene materials, neither laundering temperature nor detergent made significant impacts on the reduction of tefluthrin residues in specimens. However, with barrier laminate materials, temperature and/or detergent had significant effects on the reduction of tefluthrin residues. Under the low laundering temperature with detergent, tefluthrin residues were significantly removed from barrier laminate glove specimens.

**Pesticide Effect**

Table 36 shows the ANOVA results when pesticide type is included as a variable. Considering the whole laundering data set ($n = 144$), significant variables in explaining residue after laundering were pesticide type, glove material type, detergent, and three interaction effects. Interaction effects that were significant were glove material and pesticide type, pesticide type and detergent, and temperature and detergent.

Table 36. ANOVA for Pesticide in Glove Materials from Different Laundering Parameters

| Source | Degrees of freedom | Sum of squares | Mean square | F value | Pr>F |
|---|---|---|---|---|---|
| Pesticide | 1 | 22515742 | 22515742 | 966.72 | 0.0001 |
| Glove | 2 | 10948034 | 5474017 | 235.03 | 0.0001 |
| Temperature | 1 | 37300 | 37300 | 1.60 | 0.2080 |
| Detergent | 1 | 348943 | 348943 | 14.98 | 0.0002 |
| Measure | 1 | 2773 | 2773 | 0.12 | 0.7306 |
| Glove*pest. | 2 | 12624031 | 6312016 | 271.01 | 0.0001 |
| Glove.temp. | 2 | 27569 | 13784 | 0.59 | 0.5548 |
| Glove.detergent | 2 | 80234 | 40117 | 1.72 | 0.1827 |
| Pest.*temp. | 1 | 9998 | 9998 | 0.43 | 0.5135 |
| Pest.*detergent | 1 | 281689 | 281689 | 12.09 | 0.0007 |
| temp.*detergent | 1 | 509431 | 509431 | 21.87 | 0.0001 |
| Error | 128 | 2981227 | 23291 | | |
| Total | 143 | 50366973 | | | |

The analysis indicated that terbufos and tefluthrin contamination differed significantly ($p < 0.01$). After laundering, the mean terbufos residue in glove materials was much higher than tefluthrin residue under the same treatment conditions, as shown in Table 28 and Table 32.

**Pesticides in Laundering Solution**

Table 37 gives the amounts of pesticide found in laundering solution used for laundering glove specimens with different laundering parameters. The amount of pesticide found in laundering solution varied depending on pesticide type, glove material, laundering temperature, and detergent. The results of analysis by GC showed that the mean amount of terbufos found in laundering solution after different laundering parameter

Table 37. Pesticide Found in Laundering Solution Used for Different Laundering Parameter Treatments (ng/150 ml)

| | Terbufos | | | Tefluthrin | | |
|---|---|---|---|---|---|---|
| | Nitrile | Neoprene | B.L. | Nitrile | Neoprene | B.L. |
| <u>High temperature</u> | | | | | | |
| Det. | 485 | 322 | 2706 | 78 | 135 | 218 |
| ng/ml | 3.2 | 2.1 | 18.0 | 0.5 | 0.9 | 1.5 |
| No det. | nda[a] | 303 | 1249 | 136 | 114 | 104 |
| ng/ml | nda[a] | 2.0 | 8.3 | 0.9 | 0.8 | 0.7 |
| <u>Low temperature</u> | | | | | | |
| Det. | 315 | 265 | 1694 | 65 | 117 | 137 |
| ng/ml | 2.1 | 1.8 | 11.3 | 0.4 | 0.8 | 0.9 |
| No det. | nda[a] | 524 | 158 | 87 | 136 | 109 |
| ng/ml | nda[a] | 3.5 | 1.1 | 0.6 | 0.9 | 0.7 |

[a] no detectable amount

treatments ranged from the no detectable amount for nitrile washed without detergent at high or low temperature to 18.0 ng/ml for barrier laminate washed with detergent at high temperature, while amount of tefluthrin ranged from 0.4 ng/ml for nitrile with detergent at low temperature to 1.5 ng/ml for barrier laminate with detergent at high temperature.

As for experiment 2, the factorial analysis of variance for the entire laundering data set including both terbufos and tefluthrin (n = 144) was used to determine significant variables (Table 38). Pesticide type, glove material, detergent, and interaction between the glove materials and pesticide, temperature, and detergent were significant ($p < 0.05$), as was the interaction between pesticide and detergent. The mean amount of terbufos found in the solution was much higher than that of tefluthrin. The mean amount of pesticide found in the laundering solution with detergent was higher than that without detergent. The ANOVA showed no significant differences ($p < 0.05$) between high and low laundering temperatures on the amount of pesticide in the laundering solutions.

## Discussion

### Permeation and Contamination Levels

**Permeation and Breakthrough Time.** The findings provide evidence that terbufos or tefluthrin did not permeate glove materials into alpha-cellulose pads within the six different

Table 38. ANOVA for Pesticide Residue in Laundering Solutions with Different Laundering Parameters

| Source | Degrees of freedom | Sum of squares | Mean square | F value | Pr>F |
|---|---|---|---|---|---|
| Pesticide | 1 | 10836715 | 10836715 | 30.96 | 0.0001 |
| Glove | 2 | 11893292 | 5946646 | 16.99 | 0.0001 |
| Temperature | 1 | 1257202 | 1257202 | 3.59 | 0.0603 |
| Detergent | 1 | 3269768 | 3269768 | 9.34 | 0.0027 |
| Measure | 1 | 564 | 564 | 0.00 | 0.9680 |
| Glove*pest. | 2 | 10511501 | 5255751 | 15.01 | 0.0001 |
| Glove.temp. | 2 | 2367052 | 1183526 | 3.38 | 0.0371 |
| Glove.detergent | 2 | 4531061 | 2265531 | 6.47 | 0.0021 |
| Pest.*temp. | 1 | 975650 | 975650 | 2.79 | 0.0975 |
| Pest.*detergent | 1 | 3046479 | 3046479 | 8.70 | 0.0038 |
| Temp.*detergent | 1 | 52174 | 52174 | 0.15 | 0.7001 |
| Error | 128 | 44804711 | 350037 | | |
| Total | 143 | 93546170 | | | |

time periods and suggest that the breakthrough times of the three glove materials to granular terbufos or tefluthrin are at least more than 24 hours. Compared with permeation test data of chemical resistant glove materials exposed to liquid pesticide, as reported in the literature (Ehntholt et al., 1990; Forsberg & Keith, 1995; Moody & Ritter, 1990; Schwope et al., 1992; United States Environmental Protection Agency, 1993), breakthrough

times of the three glove materials exposed to granular terbufos or tefluthrin in this study were far longer. This difference in permeation resistance of glove materials may be explained in the following ways. First, most granular pesticides contain inert materials with low amounts of active ingredients, but liquid pesticides contain solvents and comparatively higher amounts of active ingredients. Pesticides with higher concentrations of active ingredients may break through glove materials more easily than those with low concentration of active ingredients. Second, when glove materials are contaminated by the same amount of pesticides, the contact area of glove materials with liquid pesticides is larger than that of glove materials with granular pesticides because the liquid spreads to flow over a larger area while the granular product contact is localized by its encapsulation in inert materials. Third, the carrier solvent in liquid pesticides tends to break through glove materials first and at a much higher rate than the active ingredient (Schwope et al., 1992), so the solvent enables the pesticides to move through the material.

Because granular terbufos or tefluthrin did not permeate glove materials into alpha-cellulose pads within a 24-hour time period, hypothesis one through hypothesis seven were partly revised. The examination on breakthrough time was eliminated from hypothesis one through hypothesis seven.

**Terbufos Contamination.** Hypothesis 1: There are no significant differences in contamination levels of glove materials exposed to granular terbufos at different exposure times.

Hypothesis 1 was rejected based on the statistical results as indicated in Table 11. This finding is consistent with those of Guo et al. (1998). They compared contamination levels in nitrile, neoprene, and barrier laminate glove materials after one- or two-hours exposure to granular terbufos (Counter® 15G). In their study, a significant difference in terbufos residue was found related to exposure time. Contamination levels more than doubled after two hours exposure. In the current study, Counter® 20CR was used to contaminate glove materials. Although the amount of pesticide applied in this study (0.30 g per specimen) was greater than that in the previous study (0.05 g per specimen) because of the difference in formulations as shown in Pilot Study II (Table 5) the effect of increased exposure time was similar. The longer exposure time allows more permeation.

Hypothesis 2. There are no significant differences in contamination levels among different glove materials exposed to granular terbufos.

Hypothesis 2 was rejected based on the results of statistical analysis as shown in Table 11. This finding supports the results reported by Guo et al. (1998) on contamination and permeation of chemical resistant gloves after exposure to granular pesticides. Guo and his co-authors found that the terbufos contamination was different with the three

different glove materials after exposure to granular terbufos for one or two hours. In the earlier study, the largest terbufos contamination was in neoprene specimens, followed by barrier laminate and nitrile specimens. Researchers explained that the surface character of glove materials may have contributed to the differences in contamination levels.

Another reason for the differences in terbufos contamination among different types of glove materials could be the polarity of glove materials and pesticide as well as their interrelationships. Among three glove materials, neoprene (polychloroprene) with Cl functional groups has the weakest polarity, while nitrile with CN functional groups and barrier laminate (ethylene vinyl alcohol) with the OH functional groups have stronger polarity. According to the chemical permeation theory, chemicals generally permeate materials with similar chemical polarity more easily (Raheel, 1994). Consequently, terbufos with relatively weak polarity could permeate neoprene materials more quickly, which made neoprene specimens show more contamination.

> Hypothesis 3: There is no interaction effect between glove material and exposure time on contamination levels of glove materials exposed to granular terbufos at different exposure times.

Hypothesis 3 was rejected based on the statistical results as indicated in Table 11. The finding that terbufos residues in neoprene specimens sharply increased with exposure time accords with those of Guo et al. (1998). They found that the increase

of terbufos residue in neoprene specimens with exposure time from one hour to two hours was noticeable compared with nitrile or barrier laminate specimens. As mentioned early in this chapter, the relative weak polarity of neoprene materials could be one of the reasons why terbufos in neoprene specimens increased with exposure time.

The findings that the terbufos amount in the three types of glove materials increased linearly with the increased exposure time support permeation theory. Generally, pesticide permeation through chemical protective materials obeys Fick's law (Comyn, 1985). According to permeation theory, the permeated amounts are a function of time under the conditions of continuous contact of materials with chemicals, and the total amount of chemical permeation increases linearly with time after a steady state is reached. The findings of this study mean the contamination amount may increase linearly with exposure time before breakthrough time is reached.

**Tefluthrin Contamination.** Hypothesis 4: There are no significant differences in contamination levels of glove materials exposed to granular tefluthrin at different exposure times.

Hypothesis 4 was rejected based on the statistical results indicated in Table 15. Tefluthrin contamination increased with increased exposure time. This finding is consistent with previous research (Guo et al., 1998). These results from both terbufos and tefluthrin contamination mean that when farm

workers handle granular pesticides, contamination of gloves increases with increased exposure time.

> Hypothesis 5. There are no significant differences in contamination levels among different glove materials exposed to granular tefluthrin.

Hypothesis 5 was rejected based on the results of statistical analysis, as shown in Table 15. In contrast with terbufos contamination, the largest tefluthrin contamination was found in barrier laminate, the second largest in neoprene, and the smallest in nitrile. One reason for the high levels of tefluthrin contamination might be the polarity of this glove material and the pesticides as described previously with regard to terbufos contamination. Tefluthrin with $CF_3$ and CN functional groups has a strong polarity. Therefore, tefluthrin could permeate barrier laminate materials quickly because barrier laminate with the OH functional groups also has a strong polarity. However, the polarity of nitrile and neoprene materials is relatively weak; therefore pesticides permeate these materials slowly. Another factor, the surface character of materials, might cause the difference between nitrile and neoprene in tefluthrin contamination levels. Nitrile materials have a smoother outer surface than neoprene. Consequently, tefluthrin contamination of nitrile was less than that of neoprene.

> Hypothesis 6: There is no interaction effect between glove material and exposure time on contamination levels of glove materials exposed to granular tefluthrin at different exposure times.

Hypothesis 6 was rejected based on the statistical results as indicated in Table 15. The findings that the tefluthrin amount in barrier laminate and neoprene materials increased linearly with time are consistent with permeation theory. Tefluthrin can permeate materials quickly because both pesticides and glove materials have strong polarity. Tefluthrin in barrier laminate specimens increases rapidly with increased exposure time. However, the tefluthrin contamination in nitrile materials remained almost constant as exposure time increased and the contamination amount was small. The reason may be that the nitrile material has weak polarity.

**Pesticide Effect**. Hypothesis 7: There are no significant differences in contamination levels of glove materials exposed to granular terbufos and tefluthrin.

Hypothesis 7 was rejected based on the statistical results indicated in Table 18. The differences between terbufos and tefluthrin contamination in glove materials under the same experimental conditions are likely due to the differences between terbufos and tefluthrin in physical characteristics and chemical composition such as boiling point, molecular weight, and pendant groups. According to the permeation theory, a organic compound with a higher molecular weight, more pendant groups, and a higher boiling point permeates materials more slowly than one with a lower molecular weight, less pendant groups, and a lower boiling point (Raheel, 1994). Tefluthrin has higher molecular weight, more pendant groups, and a higher melting point than terbufos. As a result, the tefluthrin

contamination in a glove specimen was much lower than terbufos contamination after the same exposure treatments. This finding indicates that the molecular weight, melting point, and chemical composition of granular pesticides may be important factors that affect the permeation and contamination of glove materials. This finding also means that when farm workers handle granular pesticides using chemical resistant gloves, gloves may be subjected to different rates of contamination and the workers can expect to receive different levels of protection from various glove materials depending on which pesticide they use.

## Effects of Cleanup Methods on Reduction of Pesticide Contamination

> **Terbufos**. Hypothesis 8: There are no significant differences in the terbufos residues in glove materials among different cleanup treatments.

Hypothesis 8 was rejected based on the statistical results indicated in Table 20, which show that cleanup methods had significant effects on reduction of terbufos residues in glove specimens. In practice, however, the effectiveness of the cleanup was a result of cleanup methods interacting with exposure time and glove material types.

The length of exposure time, 3 minutes or 30 minutes, was an important factor that affected whether terbufos residues could be removed effectively from glove specimens by the flush. An explanation is that with a three-minute exposure pesticides were sorbed at the surface of glove materials and thus could be

washed off the glove specimens easily by the flush; with 30-minute exposure, pesticides had diffused into the glove materials, thus it was difficult to remove them from glove materials by the simple flush. This finding is consistent with those of previous research studies on cleanup of glove materials exposed to granular terbufos (Guo et al., 1997; Stone et al., 1997). Stone et al. (1997) found that with a three-minute exposure to granular terbufos by the glove finger methods, contamination of neoprene and nitrile glove materials was reduced significantly by stirring the specimen in a beaker of warm water with detergent. This wash process did not significantly reduce contamination after 30-minute of petri dish exposure. In another study, Guo et al. (1997) also found that after 30-minute exposure neither stirring in a beaker, flush, nor their combination could reduce terbufos residues effectively in nitrile specimens.

Compared with the flush, the Launder-Ometer washing process provided more mechanical agitation energy and two additional rinses. As a result, the LOM significantly reduced terbufos residues in nitrile and barrier laminate glove specimens no matter whether the exposure time was 3 minutes or 30 minutes. However, pesticide redeposition may reduce the cleanup effectiveness of LOM wash because the pesticide residue washed off one side of a material may redeposit on the other side of materials during the time in the canisters. The LOM washing did

not completely remove terbufos from nitrile and barrier laminate glove specimens.

The effectiveness of the cleanup was also related to glove material. Neoprene showed worse cleanup performance than the nitrile and barrier laminate materials, especially with the 30-minute exposure time. The reason may be that although the same amount of granular terbufos was applied to any of three glove materials, the neoprene material absorbed more at a faster rate than the other two glove materials because of its specific chemical composition and physical characteristics, as mentioned earlier. In addition, since the chemical structure and polarity of neoprene materials and terbufos have some similarities, it is difficult to separate them during laundering.

**Tefluthrin.** Hypothesis 9: There are no significant differences in the tefluthrin residues in glove materials among different cleanup treatments.

Hypothesis 9 was rejected based on the statistical results, as indicated in Table 23. This means that cleanup methods significantly reduced tefluthrin residues in glove specimens. There were many similarities between tefluthrin and terbufos in the effects of cleanup methods on reduction of pesticide residues. However, there were some differences.

With three-minute exposure time, either flush or Launder-Ometer wash removed most of the tefluthrin from nitrile and neoprene specimens; pesticide residues in nitrile specimens after Launder-Ometer wash were very tiny. With 30-minute exposure time, the flush still removed 88 % of tefluthrin from

nitrile specimens; this suggests that most tefluthrin remained on the surface of the nitrile material after the 30-minute exposure. With the 30-minute exposure time, the flush did not remove tefluthrin effectively from neoprene materials, but Launder-Ometer wash significantly reduced the tefluthrin residues.

Among three types of glove materials, barrier laminate materials showed the worst cleanup performance. The reason may be that the barrier laminate materials have a strong chemical polarity, which makes them absorb more tefluthrin than the other two materials due to the attraction between barrier laminate materials and tefluthrin. Furthermore, hydrogen bonds can be formed between the O-H of the barrier laminate material and the nitrogen, oxygen, or fluorine of the tefluthrin. This bond is not as strong as a regular covalent bond, but it is still an important chemical attraction. This obstructs the removal of tefluthrin residues from barrier laminate materials by laundering.

**Pesticide Effect.** Tefluthrin residues in glove materials were much lower than terbufos after the flush or Launder-Ometer wash. In other words, tefluthrin residues could be removed from glove specimens more effectively by laundering treatments. Several researchers reported that the water solubility of pesticides might play a more important role than chemical class in the effectiveness of pesticide removal after laundering

(Easley et al., 1983; Laughlin et al., 1985). In this study, the two pesticides had similar water solubility. Therefore, the water solubility of these pesticides was not a reason for the difference between them in laundering effectiveness. Tefluthrin and terbufos, respectively, are a synthetic pyrethroid and an organophosphate that have different chemical structures. These findings provide evidence to support the those of Keaschall et al. (1986) and North Central Agricultural Experiment Stations (1988) who found that pesticide class, such as organochlorines, organophosphates, and carbamates, was one of the factors affecting laundering effectiveness in reducing pesticide contamination. According to the results of the present research study, it is possible to infer that the chemical composition of pesticides is one of the factors that affects laundering effectiveness. However, these findings should be interpreted with caution because of the limited number of specimens analyzed.

**Pesticides in Laundering Solution.** Hypothesis 10: There were no significant differences between the amount of pesticide residues found in flushing water solution and that in washing water solution.

Hypothesis 10 was rejected based on the statistical results, as indicated in Table 27. The finding that the mean amount of pesticide found in washing solution was higher than that found in flushing solution means that the Launder-Ometer washing removes more pesticide. The findings obtained from water solution on the decontamination effectiveness of two

cleanup methods are consistent with those obtained from analyses on pesticide residues in glove specimens. These results support the findings of Kim et al. (1982, 1986) where detergent gave improved cleanup because the flush had no detergent. Furthermore, flush had only kinetic agitation/flow forces while LOM gave more rigorous agitation.

The findings that the mean amount of terbufos found in laundering solution was higher than that of tefluthrin and that the mean amount of pesticide found in laundering solution with 3-minute exposure was lower than that with 30-minute exposure time supports the findings from analyses on pesticide residues in glove specimens. In addition, significant differences also were found among the three different glove materials in the amount of pesticide found in laundering solution. This finding is similar to that obtained from the analyses on pesticide residues in glove specimens.

Traditionally, in studies on the effectiveness of laundering for decontamination, the pesticide residues in fabric specimens were examined to determine contamination levels both before and after laundering, but no direct measures were made of the amount of pesticide in the wash water solution. However, the analysis of the pesticide residues in laundering water solution in this research has determined directly how much pesticide was in the water solution after laundering. In this study, the decontamination findings were strengthened because

the residue in both the glove material and the water were determined.

In theory, the amount of pesticide applied to a glove specimen as contamination before laundering should be equal to the sum of the residue found in a glove specimen after laundering and the residue found in the laundering water solution. In this study, the first value was more than the sum of the following two values. The difference might be due to many factors. First, the pesticide residues in laundering water solution could not be extracted completely by solvent with the solid phase extraction techniques since the recovery rate of tefluthrin from water solution was about 76% and that of terbufos was about 90%. Second, the pesticide residues in rinsing water solution were not analyzed. Third, some pesticide residues might volatilize away during preparation, laundering, and storage procedures. This assumption based on the findings of a previous study on the granular terbufos contamination of cotton denim (Stone et al., 1992a). Stone et al. found that, although there was not direct physical contact between the cotton fabrics and the granules in a covered petri dish, the fabrics still were contaminated by terbufos. They concluded that contamination of fabrics was due to volatilization of terbufos. Fourth, during the experimental procedures the water solution was transferred among different containers, allowing the possibility of loss of pesticides due to adsorption.

These findings may raise some environmental and health concerns. In most farm families, laundering waste water is drained directly into septic systems and lateral lines. This waste water, containing low levels of pesticides, adds to the contamination load in the nearby environment. Lateral lines are deeper than the level at which pesticides are applied for crop management and this contamination therefore may represent a threat to ground water in some localities. Potential health risks to launderers from volatilization or adsorption of pesticide residues during the laundering process from handling the contaminated gloves are unknown, but launderers are advised to wear protective gloves in handling contaminated clothing.

## Effects of Laundering Parameters on Reduction of Pesticide Contamination

> **Terbufos**. Hypothesis 11: There are no significant differences in the amount of terbufos residues in glove materials after laundering with the use of detergents and without detergents.
>
> Hypothesis 12: There are no significant differences in the amount of terbufos residues in glove materials after laundering at different laundering temperatures.

Hypothesis 11 was rejected based on the statistical results in Table 29. Detergent had significant effects on the removal of terbufos residues from glove materials after laundering. This finding supports the previous findings that laundering with detergent removed more pesticide residues in fabrics than laundering without detergent (Kim et al., 1982, 1986, 1988;

Laughlin, 1993; Raheel, 1987). In the present study, after the 30-minute exposure some terbufos has begun to diffuse into the matrix of glove materials. These findings imply that detergent can still play an active role in the decrease of pesticide residues in glove materials although the pesticide diffusion has taken place. However, the effectiveness of decontamination by laundering is strongly dependent on the interaction of the specific pesticides and glove materials. In this study, although detergent significantly affected the removal of terbufos residues from nitrile or barrier laminate materials, detergent did not have a significant effect on the removal of terbufos residues from neoprene glove materials with laundering. The reason may be that with a large amount of terbufos diffused into the matrix of neoprene glove materials, the laundering time was too short to permeate the molecular matrix and reach all of it, so that the LOM laundering method could not reduce the terbufos residues from neoprene glove materials.

Hypothesis 12 was not rejected based on the statistical results in Table 29. There were no significant differences between $30^0$C and $60^0$C laundering temperature in the removal of terbufos residues from glove materials. When laundering glove materials, although increasing the temperature might accelerate desorption, the higher temperature could cause the glove materials to swell; swelling of the glove materials might entrap pesticide residue, inhibiting decontamination in laundering.

Previous research on the effect of water temperature in laundering pesticide contaminated clothing has been inconclusive. Some research has suggested that an increase in laundering temperature generally improves pesticide removal from fabrics (Easley et al., 1982; Easter, 1983; Lillie et al., 1981, 1982). However, other researchers found that laundering temperature did not lead to a significant difference in the removal of pesticide residues from fabrics (Kim et al., 1982, 1986; Olsen et al., 1986; Raheel, 1987), especially when laundering temperatures were within limited ranges such as between 49$^0$C and 60$^0$C. The latter work is supported by the findings of the present study. The explanation may be that the water solubility of pesticides varies or keeps constant with water temperature depending on the characteristics of specific pesticides (Moran, 1994), which affects effectiveness of pesticide removal from fabrics and glove materials.

**Tefluthrin**. Hypothesis 13: There are no significant differences in the amount of tefluthrin residues in glove materials after laundering with the use of detergents and without detergents.

Hypothesis 14: There are no significant differences in the amount of tefluthrin residues in glove materials after laundering at different laundering temperatures.

Hypotheses 13 and 14 respectively were rejected based on the statistical results in Table 33. Compared to terbufos, tefluthrin was easier to remove from glove materials. After each laundering treatment, most tefluthrin residues were removed from the nitrile and neoprene specimens; only very small amount

of tefluthrin residues remained in nitrile and neoprene specimens. Since tefluthrin was easy to remove from nitrile and neoprene glove specimens, laundering temperature and detergent did not play an important role in the removal of tefluthrin from glove specimens. Therefore, the differences in temperature or whether detergent was used did not make a significant difference on the reduction of tefluthrin residues in nitrile and neoprene specimens. This suggests that pesticide composition has a greater impact on the reduction of pesticide residues than does either laundering temperature or detergent.

However, significant differences were found in tefluthrin residues in barrier laminate glove materials. Tefluthrin residues in barrier laminate after laundering with detergent were lower than those laundered without detergent. This finding supports the previous findings that laundering with detergent removes more pesticide residue in fabrics (Kim et al., 1982, 1986, 1988; Laughlin, 1993; Raheel, 1987).

Tefluthrin residues in barrier laminate after laundering at $30^0$C were lower than those at $60^0$C. Barrier laminate materials are not heat resistant. The higher temperature might cause the laminate structure to loosen or swell, which could entrap pesticide residue, obstructing effective removal of pesticides by laundering. According to laundering theory, the effectiveness of laundering is the interaction result of chemical energies, mechanical energies, and thermal energies produced respectively by detergent, mechanical agitation, and

wash temperature (Laughlin, 1993). Thus, when laundering temperature is lower, other energies such as using detergent helps maintain the detersive action. This finding is consistent with those concerning removal of terbufos from barrier laminates in this study. Although no significant differences were found in terbufos residues between 30$^0$C and 60$^0$C laundering temperatures, considering three types of glove materials as a whole data set, terbufos residues in barrier laminate after laundering at 30$^0$C were lower than those at 60$^0$C. This means that 30$^0$C laundering temperature is better than 60$^0$C in effectiveness of decontamination from barrier laminate materials no matter whether terbufos or tefluthrin is used.

**Pesticides in Laundering Solution**. Hypothesis 15: There are no significant differences in the amount of pesticide residues in laundering water solution with the use of detergents and without detergents.

Hypothesis 16: There are no significant differences in the amount of pesticide residues in laundering water solution between different laundering temperatures.

Hypothesis 15 was rejected based on the statistical results as indicated in Table 38. The finding that pesticides in laundering solutions with detergent were much higher than those without detergent shows that laundering with detergent removes pesticide residues from glove materials more effectively than does laundering without detergent. This finding is consistent with those obtained from analyses on pesticide residues in glove specimens in this study. Based on the statistical analysis of data from laundering solutions (Table 38), pesticide type and

glove materials had greater effects on pesticide removal from glove materials than did detergent use. This finding is consistent with those obtained from statistical analyses on the data of pesticide residues in glove specimens (Table 36) in this study.

Hypothesis 16 was not rejected based on the statistical results indicated in Table 38. There were no significant differences between $30^0$C and $60^0$C laundering temperatures in the amount of pesticide residues in laundering solution. This result is consistent with the previous findings in which laundering temperature did not significantly affect the removal of pesticide residues from fabrics (Kim et al., 1982, 1986; Olsen et al., 1986; Raheel, 1987). This results also supports similar findings from analyses on pesticide residues in glove specimens in this study.

# CHAPTER 5. CONCLUSIONS

This final chapter states the conclusions of this study. In addition, implications for pesticide applicators and recommendations for further research are introduced based on findings of this study.

## Conclusions

### Permeation and Contamination Levels

The present study offers evidence that terbufos or tefluthrin did not permeate glove materials into alpha-cellulose pads within the six different time periods. The findings mean that the breakthrough times of the three glove materials to granular terbufos or tefluthrin were at least more than 24 hours. Thus, the findings can lead us to assume that three types of gloves used in this study could protect farm workers from direct exposure effectively for at least 24 hours when they handle granular terbufos or tefluthrin with the proper work methods.

The three types of glove materials showed different contamination levels with exposure to the two different pesticides. The largest terbufos contamination was found in neoprene specimens, the second-largest in barrier laminate, and the smallest in nitrile specimens. However, the largest tefluthrin was in barrier laminate, followed by neoprene and

nitrile. The three glove materials provided a different degree of efficiency of protection from the two pesticides. Nitrile and barrier laminate seem to offer better resistance to terbufos contamination, while nitrile and neoprene provide better resistance to tefluthrin contamination by showing low residues before cleanup. The differences in pesticide contamination among different types of glove materials might be attributed to the polarity of glove materials and pesticides. Chemicals tend to permeate materials of a similar polarity more rapidly.

Exposure time had significant effects on contamination in glove materials for both terbufos and tefluthrin. There were strong linear relationships between terbufos contamination and exposure time in each type of glove material. With a longer exposure time, more terbufos residue was found in the glove materials. After 24 hours, compared with nitrile or barrier laminate specimens, the total contamination in neoprene specimens was four times greater. Similarly, the amounts of tefluthrin residues in glove materials varied with exposure time. There were linear relationships between exposure time and tefluthrin contamination in barrier laminate and neoprene materials. As exposure time increased, more tefluthrin contamination was found in barrier laminate and neoprene materials. In contrast, no linear relationship was found between tefluthrin contamination and exposure time in nitrile materials. The tefluthrin residues in nitrile materials were very small and almost remained constant as exposure time

increased from one hour to 24 hours. Compared with the neoprene glove material, the tefluthrin residue in barrier laminate material was ten times greater after 24 hours. These findings suggest that when farm workers handle granular pesticides for a longer time, their glove contamination increases. When using gloves, the longer the exposure time, the greater the risks.

The pesticides composition had significant effects on glove material contamination levels. The contamination levels of terbufos in glove materials were much higher than those of tefluthrin under the same exposure treatment. It seems that the chemical composition of granular pesticides might be a critical factor that influences the permeation and contamination of glove materials. These findings imply that the potential contamination levels of glove materials are pesticide-specific. When farm workers handle different granular pesticides wearing chemical resistant gloves, the gloves may be contaminated at different levels. Workers can expect to receive different levels of protection from gloves depending on which pesticide they use.

**Cleanup Methods**

Cleanup methods had significant effects on reduction of pesticide residues in glove specimens. The effectiveness of cleanup methods was related to the interactions of cleanup methods with exposure time and glove materials.

The length of exposure time significantly affected the reduction of pesticide contamination in glove specimens. In general, after the three-minute exposure, pesticides might be sorbed only at the surface of glove specimens; thus, either simple flush or Launder-Ometer laundering could reduce pesticide residues in glove specimens significantly. After 30-minute exposure, however, pesticides might be diffused through glove specimens; thus, only Launder-Ometer laundering could remove pesticide residues from glove specimens significantly. However, except for a case of nitrile materials exposed to tefluthrin, after the LOM cleanup, a certain amount of residues may remain within glove materials. The health risks for wearing the reused gloves after their cleanup are unknown.

The effectiveness of the cleanup also was related to glove material. Among the three types of glove materials, nitrile materials showed the best cleanup performance, especially after exposure to tefluthrin. Either simple flush or Launder-Ometer laundering could reduce tefluthrin residues significantly no matter whether the exposure time was 3 minutes or 30 minutes. After Launder-Ometer laundering tefluthrin residues in nitrile specimens were very tiny. In contrast, with the exposure to granular terbufos, neoprene showed the worst cleanup performance. After the 30-minute exposure, even Launder-Ometer laundering could not reduce terbufos residues in neoprene specimens effectively. After the 30-minute exposure, the Launder-Ometer laundering could remove only about half of the

tefluthrin from barrier laminate specimens while the same laundering methods could remove most of tefluthrin from nitrile or neoprene specimens. As a result, nitrile gloves are highly recommended for both terbufos and tefluthrin. In addition, barrier laminate gloves also are recommended for terbufos and neoprene gloves for tefluthrin. The rank order of the three glove materials in terbufos or tefluthrin residue retention is consistent with that of the three glove materials in contamination levels. These findings show that the more contamination glove materials receive, the more difficult it is to remove it.

The findings of this study show that tefluthrin residues in glove materials were much lower than terbufos residues after laundering treatments. This means that tefluthrin residues could be removed from glove specimens more effectively by laundering treatments. These findings show that the chemical composition and characteristics of granular pesticides affect pesticide residue retention in glove specimens after laundering. However, since only two granular pesticides were examined in this study, the findings should be interpreted with some caution and need to be confirmed by further studies.

Pesticides were found in the laundering solutions. The amount of pesticide found in laundering solution varied with pesticide type, cleanup method, glove material, and exposure time. The amount of pesticide found in washing solution was higher than that found in flushing solution. This might be

attributed to the fact that the LOM wash had a longer wash time and provided more mechanical agitation. In addition, significant differences in the amount of pesticides in laundering solution were found respectively between terbufos and tefluthrin, between 3-minute and 30-minute exposure time, and among the three different glove materials. The findings obtained from laundering solution generally support those from analyses on pesticide residues remaining in glove specimens. It is unclear whether there are potential health and environmental risks associated with the amount of pesticide remaining in the laundering water solution.

**Laundering Parameters**

Detergent had significant effects on reduction of pesticide residues in glove materials; however, laundering temperature did not affect significantly the removal of pesticide residues from glove specimens. In general, the reduction of pesticide residue in glove materials by laundering is pesticide-specific and related to pesticides, glove materials, and laundering parameters, as well as their interaction.

Detergent had significant effects on the removal of terbufos residues from glove materials by laundering; the mean amount of terbufos residues in glove specimens with detergent was lower than that without detergent. However, the effectiveness of decontamination by laundering with detergent is material-specific. In this study, although detergent

significantly affected the removal of terbufos residues from nitrile or barrier laminate materials, detergent did not have a significant effect on the removal of the terbufos residues from neoprene glove materials by laundering. On the other hand, there were no significant differences between $30^0$C and $60^0$C laundering temperature in the removal of terbufos residues from glove materials by laundering.

The findings show that detergent and laundering temperature had significant effects on the reduction of tefluthrin residues in glove specimens after laundering. However, significant differences among different laundering parameters in tefluthrin residues in glove specimens were mainly from barrier laminate materials since most tefluthrin residues were removed from nitrile and neoprene specimens after each laundering treatment. Tefluthrin residues in barrier laminate after laundering with detergent were lower than those without detergent. This means that laundering with detergent could remove more tefluthrin residues from barrier laminate glove materials. More tefluthrin residues were removed from barrier laminate glove specimens at $30^0$C laundering temperature than at $60^0$C. A similar result was found in the decontamination of terbufos from the barrier laminate materials. This means that $30^0$C laundering temperature was better than $60^0$C in effectiveness of decontamination from barrier materials no matter whether terbufos or tefluthrin is used.

In this study, a significant difference in the amount of pesticides in laundering water solution was found between the use of detergents and the absence of detergents. Pesticides in laundering solution with detergent were much higher than that without detergent, which means laundering with detergent could remove pesticide residues from glove materials more effectively than laundering without detergent. No significant differences in the amount of pesticide residues in laundering solution were found between $30^0$C and $60^0$C laundering temperature, which implies that laundering temperature did not have significant effects on removal of pesticide residues from glove materials.

## Implications

The findings of this study offer several implications for pesticide applicators and farm workers. First, since the contamination levels and the cleanup effectiveness of glove materials are pesticide-specific, farm workers should select chemical resistant gloves based on the granular pesticides they would handle. Specifically, according to the findings of this study, nitrile or barrier laminate gloves should be chosen for handling granular terbufos while nitrile or neoprene gloves should be selected for handling granular tefluthrin.

Second, when farm workers mix and load granular pesticides, it is critical to shorten the time of direct glove contact with the pesticides. Pesticide residues should be removed from gloves as quickly as possible after wear, because with the

increased exposure time, contamination in gloves increases linearly. It is more difficult to remove pesticide residues from the contaminated gloves by laundering after long exposure. It might be a good precautionary practice to replace gloves after a short interval during long-time operation to avoid long exposure. Also, if these gloves would be used again, they should be rinsed under running water immediately after use.

Third, after wear the contaminated gloves should be washed with warm water and a strong detergent under intensive mechanical agitation as soon as possible if these gloves are intended for reuse. Pre-rinse or pre-flush before washing and repeated rinse after washing is also recommended to maximize the effectiveness of decontamination.

Fourth, farm workers should be very cautious about wearing gloves refurbished by laundering. According to the findings of this study, a certain amount of pesticide residue remained in the matrix of glove materials after the granules on the surface of specimens were removed even after the specimens were washed and rinsed by a Launder-Ometer. Although the terbufos or tefluthrin did not permeate glove materials into alpha-cellulose pads within the 24-hour time period, it is unclear if these pesticide residues absorbed in the matrix of glove specimens eventually would continue to diffuse or even permeate through glove materials. Therefore, it is strongly recommended that when handling granular pesticides, farm workers should replace their gloves frequently or use disposable gloves. For toxic

pesticides, gloves are important to minimize health risks and prevent hand contamination.

Finally, the findings suggested that practical methods of the choice, use, and decontamination of chemical resistant gloves can reduce possible hand exposure to pesticides. Therefore, these findings on pesticide contamination and cleanup of gloves are very important to farm workers and pesticide applicators.

## Recommendations for Further Research

The finding that the length of exposure time significantly affected the reduction of pesticide contamination in glove materials by laundering suggests directions for the further study. The length of time the flush method remains useful in reducing contamination is unknown. Additionally, the extent of the time period in which the LOM is useful is unknown. Further, study on the effectiveness of cleanup methods should include additional exposure time periods such as 10 and 20 minutes or times beyond 30 minutes, such as one or two hours. Such studies on the effect of exposure time on laundering effectiveness are of considerable importance because if acceptable levels of pesticide removal are not obtained gloves cannot be reused.

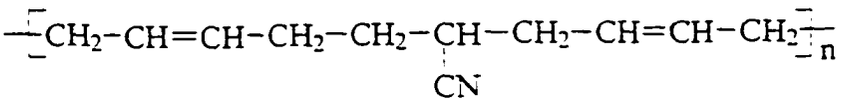
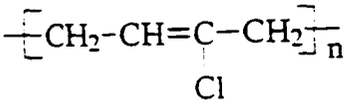
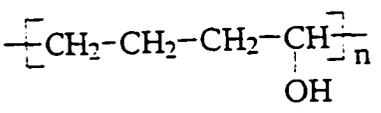
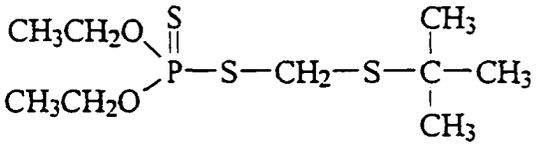
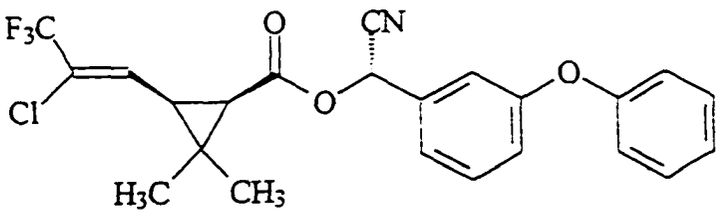
Further study also could investigate the effects of detergent type and concentration on the removal of pesticides from glove materials. This research showed heavy duty liquid

Tide® was useful in reducing contamination, but other detergents may not be as helpful.

A field study on pesticide exposure and cleanup of gloves would be a logical continuation of this research. In a field study, farm workers or pesticide applicators might wear different types of chemical resistant gloves for a set period of time as they handle or/and apply pesticides. The effects of pesticide type, glove material, exposure time, and cleanup protocol on contamination levels in gloves under the field situation would be examined. After the wear and exposure time, the contaminated gloves could be cleaned by set protocols that include both a flush and washing process using detergent as one treatment. Such a study is of practical importance since it would examine pesticide exposure levels and the effectiveness of cleanup methods of gloves under the "real world" conditions of agricultural production.

# APPENDIX A: GLOVE MATERIAL AND PESTICIDE STRUCTURAL FORMULAS

Table A1. Glove Material and Pesticide Structural Formulas

| Material | Structural formula |
|---|---|
| <u>Glove material</u> | |
| Nitrile rubber |  |
| Neoprene (Polychloroprene) |  |
| Barrier laminate (Ethylene vinyl alcohol) |  |
| <u>Pesticide</u> | |
| Terbufos |  |
| Tefluthrin |  |

# APPENDIX B: GLOVE SPECIMEN PREPARATION AND CONTAMINATION

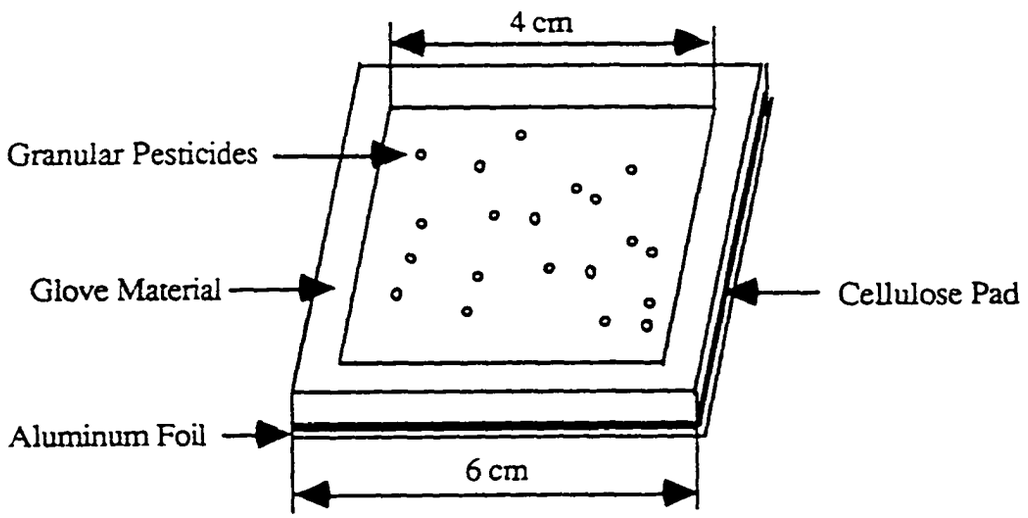



Figure B. Glove Specimen Preparation and Contamination

# APPENDIX C: RAW DATA

Table C1. Effect of Exposure Time on Terbufos Remaining in Three Glove Materials (ng/cm$^2$)

| Exposure time | Glove materials | | |
|---|---|---|---|
| | Nitrile | Neoprene | Barrier laminate |
| 1 Hour | | | |
| | 1385.63 | 6524.38 | 2926.88 |
| | 1340.63 | 7016.25 | 2681.25 |
| | 502.50 | 5854.38 | 3061.25 |
| | 469.38 | 4938.13 | 3351.25 |
| | 413.13 | 4535.63 | 2926.88 |
| | 391.25 | 3820.63 | 3284.38 |
| Mean | 750.42 | 5448.23 | 3038.65 |
| 2 Hours | | | |
| | 781.25 | 12423.13 | 5473.75 |
| | 882.50 | 10770.00 | 5720.00 |
| | 692.50 | 16511.88 | 5429.38 |
| | 603.13 | 15484.38 | 5094.38 |
| | 1285.00 | 15640.63 | 5228.75 |
| | 1251.25 | 11685.63 | 5474.38 |
| Mean | 915.94 | 13752.60 | 5403.44 |
| 4 Hours | | | |
| | 2703.75 | 33068.75 | 10658.13 |
| | 2558.13 | 36531.88 | 9205.63 |
| | 2245.63 | 38543.13 | 9853.75 |
| | 2435.63 | 36420.63 | 9228.13 |
| | 1564.38 | 31616.25 | 10501.25 |
| | 1586.25 | 35191.25 | 10412.50 |
| Mean | 2182.29 | 35228.65 | 9976.56 |

Table C1 (continued)

| Exposure time | Glove materials | | |
|---|---|---|---|
| | Nitrile | Neoprene | Barrier laminate |
| 8 Hours | | | |
| | 4468.75 | 42453.13 | 13797.50 |
| | 4200.63 | 41112.50 | 12289.38 |
| | 7552.50 | 54071.88 | 13685.63 |
| | 7775.63 | 54071.88 | 11742.50 |
| | 7596.88 | 51837.50 | 12456.25 |
| | 8781.25 | 53625.00 | 13630.00 |
| Mean | 6729.27 | 49528.65 | 12933.54 |
| 16 Hours | | | |
| | 18880.63 | 111718.75 | 18321.88 |
| | 19886.25 | 98759.38 | 19662.50 |
| | 6591.25 | 90715.63 | 20109.38 |
| | 6591.25 | 87140.63 | 15183.13 |
| | 23598.75 | 87587.50 | 24578.13 |
| | 20780.00 | 98312.50 | 19886.25 |
| Mean | 16054.69 | 95705.73 | 19623.54 |
| 24 Hours | | | |
| | 37314.38 | 134062.50 | 34633.13 |
| | 36867.50 | 124008.13 | 34186.25 |
| | 39660.00 | 138531.25 | 37090.63 |
| | 33400.00 | 134062.50 | 37984.38 |
| | 23125.63 | 140765.63 | 34409.38 |
| | 23795.63 | 137414.38 | 31951.88 |
| Mean | 32360.52 | 134807.40 | 35042.60 |

Table C2. Effect of Exposure Time on Tefluthrin Remaining in Three Glove Materials ($ng/cm^2$)

| Exposure time | Glove materials | | |
|---|---|---|---|
| | Nitrile | Neoprene | Barrier laminate |
| 1 Hour | | | |
| | 27.38 | 184.93 | 754.06 |
| | 27.38 | | |
| | 35.63 | 182.25 | 725.31 |
| | 31.50 | | |
| | 61.69 | 85.93 | 614.06 |
| | 61.69 | | |
| Mean | 40.88 | 151.04 | 697.81 |
| 2 Hours | | | |
| | 30.31 | 269.25 | 1048.94 |
| | 36.88 | 266.88 | 904.19 |
| | 34.69 | 195.31 | 1027.06 |
| | 34.69 | 190.94 | 1012.75 |
| | 33.69 | 177.19 | 915.06 |
| | 39.06 | 156.25 | 846.38 |
| Mean | 34.89 | 209.30 | 959.06 |
| 4 Hours | | | |
| | 43.44 | 168.94 | 1453.93 |
| | 49.88 | 168.94 | 1844.56 |
| | 99.88 | 185.81 | 1425.81 |
| | 95.50 | 160.50 | 1308.63 |
| | 50.63 | 224.63 | 1464.88 |
| | 52.63 | 209.97 | 1523.44 |
| Mean | 65.32 | 185.84 | 1503.54 |

Table C2 (continued)

| Exposure time | Glove materials | | |
|---|---|---|---|
| | Nitrile | Neoprene | Barrier laminate |
| 8 Hours | | | |
| | 65.44 | 230.50 | 3906.25 |
| | 63.38 | 210.94 | 3695.31 |
| | 86.56 | 389.63 | 4434.06 |
| | 73.88 | 426.25 | 3959.06 |
| | 52.81 | 213.75 | 3695.31 |
| | 52.81 | 183.00 | 3642.31 |
| Mean | 65.81 | 275.68 | 3888.72 |
| 16 Hours | | | |
| | 39.06 | 269.56 | 4687.50 |
| | 39.06 | 238.31 | 4375.00 |
| | 58.63 | 523.43 | 4687.50 |
| | 43.00 | 507.81 | 4687.50 |
| | 62.50 | 712.88 | 4687.50 |
| | 61.19 | 781.25 | 5039.06 |
| Mean | 50.57 | 505.54 | 4694.01 |
| 24 Hours | | | |
| | 35.19 | 449.25 | 5546.88 |
| | 35.19 | 535.19 | 5468.75 |
| | 63.81 | 578.69 | 5429.69 |
| | 69.00 | 578.69 | 5078.13 |
| | 40.38 | 585.94 | 5234.38 |
| | 46.87 | 551.75 | 4960.94 |
| Mean | 48.40 | 546.59 | 5286.46 |

Table C3. Effect of Cleanup Methods and Exposure Time on Terbufos Remaining in Three Glove Materials ($ng/cm^2$)

| | Nitrile | | | Neoprene | | | Barrier laminate | | |
|---|---|---|---|---|---|---|---|---|---|
| | Control | Flush | Wash | Control | Flush | Wash | Control | Flush | Wash |
| 3 Minutes | | | | | | | | | |
| | 75.00 | 14.38 | 23.75 | 340.63 | 70.00 | 402.50 | 391.25 | 238.13 | 201.25 |
| | 91.25 | 27.50 | 28.75 | 366.25 | 87.50 | 368.75 | 380.00 | 360.63 | 173.13 |
| | 85.00 | 33.75 | 72.50 | 298.75 | 91.88 | 335.00 | 296.25 | 218.75 | 173.13 |
| | 102.50 | 27.50 | 42.50 | 329.38 | 87.50 | 298.13 | 357.50 | 161.88 | 161.88 |
| | 70.63 | 29.38 | 6.88 | 266.25 | 180.00 | 268.13 | 346.25 | 245.00 | 184.38 |
| | 54.38 | 30.63 | 6.25 | 283.75 | 207.50 | 208.75 | 318.13 | 245.00 | 178.75 |
| Mean | 79.79 | 27.19 | 30.10 | 314.17 | 120.73 | 313.54 | 348.23 | 244.90 | 178.75 |
| 30 Minutes | | | | | | | | | |
| | 673.75 | 472.50 | 28.13 | 2111.25 | 1382.50 | 1512.50 | 1262.50 | 1137.50 | 770.63 |
| | 580.63 | 487.50 | 41.25 | 2279.38 | 1650.63 | 1800.00 | 1072.50 | 904.38 | 726.25 |
| | 286.25 | 548.75 | 157.50 | 1608.75 | 2630.63 | 1776.25 | 1237.50 | 1108.13 | 692.50 |
| | 274.38 | 867.50 | 161.25 | 2100.63 | 2852.50 | 2312.50 | 1256.25 | 1195.63 | 748.75 |
| | 359.38 | 332.50 | 218.13 | 1865.63 | 1324.38 | 1810.00 | 1016.88 | 1365.00 | 736.25 |
| | 413.13 | 267.50 | 236.25 | 2033.13 | 1505.00 | 1977.50 | 1005.63 | 1137.50 | 692.50 |
| Mean | 431.25 | 496.04 | 140.42 | 2000.21 | 1890.94 | 1864.79 | 1141.88 | 1141.35 | 727.81 |

Table C4. Effect of Cleanup Methods and Exposure Time on Tefluthrin Remaining in Three Glove Materials ($ng/cm^2$)

| | Nitrile | | | Neoprene | | | Barrier laminate | | |
|---|---|---|---|---|---|---|---|---|---|
| | Control | Flush | Wash | Control | Flush | Wash | Control | Flush | Wash |
| 3 Minutes | | | | | | | | | |
| | 69.56 | 4.75 | 0.14 | 57.81 | 23.44 | 4.38 | 210.94 | 125.00 | 53.12 |
| | 64.88 | 4.75 | 0.14 | 57.81 | 23.94 | 4.38 | 215.63 | 139.06 | 55.63 |
| | 31.25 | 2.44 | 0.23 | 96.13 | 13.69 | 3.75 | 267.19 | 125.00 | 60.63 |
| | 38.31 | 2.88 | 0.13 | 98.44 | 13.69 | 3.75 | 253.13 | 134.38 | 66.88 |
| | 73.44 | 4.75 | 0.22 | 107.81 | 21.88 | 11.25 | 243.75 | 171,88 | 41.25 |
| | 66.43 | 4.75 | 0.23 | 121.88 | 21.88 | 11.25 | 264.06 | 157.81 | 42.50 |
| Mean | 57.31 | 4.05 | 0.18 | 89.98 | 19.75 | 6.46 | 242.45 | 142.19 | 53.33 |
| 30 Minutes | | | | | | | | | |
| | 50.00 | 7.63 | 0.17 | 271.88 | 84.38 | 41.75 | 546.87 | 435.94 | 275.31 |
| | 57.06 | 7.19 | 0.19 | 271.88 | 66.25 | 44.00 | 621.88 | 457.81 | 275.31 |
| | 78.94 | 8.81 | 0.14 | 91.44 | 25.19 | 8.43 | 675.00 | 489.06 | 275.31 |
| | 78.94 | 9.63 | 0.14 | 103.13 | 25.44 | 9.25 | 675.00 | 493.75 | 271.56 |
| | 60.19 | 6.94 | 0.10 | 74.31 | 299.56 | 6.00 | 700.00 | 526.56 | 267.81 |
| | 57.81 | 7.19 | 0.14 | 74.31 | 319.56 | 4.00 | 728.13 | 526.56 | 260.50 |
| Mean | 63.82 | 7.90 | 0.15 | 149.39 | 136.73 | 18.91 | 553.65 | 488.28 | 270.97 |

Table C5. Effect of Laundering Temperature and Detergent on Terbufos Remaining in Three Glove Materials ($ng/cm^2$)

| | | Detergent | | No detergent | |
|---|---|---|---|---|---|
| | Control | Low tem. | High tem. | Low tem. | High tem. |
| Nitrile | | | | | |
| | 673.75 | 215.63 | 28.12 | 787.50 | 538.75 |
| | 580.63 | 233.75 | 41.25 | 796.25 | 445.63 |
| | 286.25 | 108.75 | 157.50 | 210.63 | 409.38 |
| | 274.38 | 125.00 | 161.25 | 280.00 | 416.88 |
| | 359.38 | 65.63 | 218.13 | 320.00 | 347.50 |
| | 413.13 | 116.25 | 236.25 | 380.00 | 498.75 |
| Mean | 431.25 | 144.17 | 140.42 | 462.40 | 442.81 |
| Neoprene | | | | | |
| | 2111.25 | 1330.00 | 1512.50 | 1505.00 | 1435.00 |
| | 2279.38 | 1330.00 | 1800.00 | 1382.50 | 1601.25 |
| | 1608.75 | 1041.25 | 1776.25 | 1977.50 | 1618.75 |
| | 2100.63 | 1207.75 | 2312.50 | 1662.50 | 1338.75 |
| | 1865.63 | 1548.75 | 1810.00 | 2388.75 | 1505.00 |
| | 2033.13 | 1531.25 | 1977.50 | 2240.00 | 1417.50 |
| Mean | 1999.80 | 1331.50 | 1864.80 | 1859.40 | 1486.00 |
| Barrier laminate | | | | | |
| | 1262.50 | 402.50 | 770.63 | 945.00 | 752.50 |
| | 1072.50 | 376.25 | 726.25 | 936.25 | 691.25 |
| | 1237.50 | 507.50 | 692.50 | 787.50 | 743.75 |
| | 1256.25 | 577.50 | 748.75 | 796.25 | 717.50 |
| | 1016.88 | 490.00 | 736.25 | 761.25 | 743.75 |
| | 1005.63 | 455.00 | 692.50 | 726.25 | 735.00 |
| Mean | 1141.88 | 468.13 | 727.81 | 825.42 | 722.19 |

tem. = temperature

Table C6. Effect of Laundering Temperature and Detergent on Tefluthrin Remaining in Three Glove Materials ($ng/cm^2$)

| | | Detergent | | No detergent | |
|---|---|---|---|---|---|
| | Control | Low tem. | High tem. | Low tem. | High tem. |
| Nitrile | | | | | |
| | 50.00 | 0.25 | 0.17 | 1.56 | 0.11 |
| | 57.06 | 0.21 | 0.19 | 1.50 | 0.17 |
| | 78.94 | 0.58 | 0.14 | 0.81 | 0.26 |
| | 78.94 | 0.56 | 0.14 | 0.81 | 0.22 |
| | 60.19 | 0.33 | 0.10 | 0.81 | 0.25 |
| | 57.81 | 0.38 | 0.14 | 1.00 | 0.26 |
| Mean | 63.82 | 0.39 | 0.15 | 1.08 | 0.21 |
| Neoprene | | | | | |
| | 271.88 | nda | 8.44 | 28.75 | 13.31 |
| | 271.88 | nda | 9.25 | 28.75 | 17.06 |
| | 91.44 | nda | 41.75 | 16.50 | 6.63 |
| | 103.13 | nda | 44.00 | 16.50 | 10.00 |
| | 74.31 | nda | 6.00 | nda | 16.63 |
| | 74.31 | nda | 4.00 | nda | 18.31 |
| Mean | 147.82 | nda | 18.91 | 15.08 | 13.66 |
| Barrier laminate | | | | | |
| | 546.88 | 159.94 | 275.31 | 266.75 | 226.25 |
| | 621.88 | 167.19 | 275.31 | 259.25 | 247.00 |
| | 675.00 | 159.94 | 275.31 | 282.06 | 218.00 |
| | 675.00 | 174.44 | 271.56 | 282.06 | 232.50 |
| | 700.00 | 188.94 | 267.81 | 228.63 | 232.50 |
| | 728.13 | 181.75 | 260.50 | 224.88 | 254.38 |
| Mean | 657.81 | 172.03 | 270.97 | 257.27 | 235.10 |

tem. = temperature

Table C7. Effect of Cleanup Methods and Exposure Time on Terbufos in Laundering Solution (ng/150 ml)

| | Nitrile | | Neoprene | | Barrier laminate | |
|---|---|---|---|---|---|---|
| | Flush | Wash | Flush | Wash | Flush | Wash |
| 3 Minutes | | | | | | |
| | 161 | 373 | 336 | 157 | 123 | 85 |
| | 179 | 493 | 370 | 142 | 123 | 85 |
| | 358 | 241 | 252 | 190 | 151 | 103 |
| | 411 | 174 | 196 | 246 | 140 | 85 |
| | 151 | 119 | 273 | nda | nda | 123 |
| | 123 | 142 | 273 | nda | nda | 128 |
| Mean | 232 | 257 | 283 | 123 | 90 | 102 |
| 30 Minutes | | | | | | |
| | 314 | 364 | 291 | 333 | 308 | 1915 |
| | 325 | 370 | 246 | 286 | 297 | 2296 |
| | 121 | 499 | 626 | 373 | 146 | 701 |
| | 108 | 375 | 611 | 314 | 157 | 784 |
| | 129 | 703 | 146 | 280 | 84 | 4928 |
| | 112 | 596 | 196 | 347 | 56 | 5611 |
| Mean | 185 | 485 | 353 | 322 | 175 | 2706 |

Table C8. Effect of Cleanup Methods and Exposure Time on Tefluthrin in Laundering Solution (ng/150 ml)

| | Nitrile | | Neoprene | | Barrier laminate | |
|---|---|---|---|---|---|---|
| | Flush | Wash | Flush | Wash | Flush | Wash |
| 3 Minutes | | | | | | |
| | 194 | 118 | 122 | 281 | 61 | 104 |
| | 168 | 96 | 112 | 288 | 64 | 108 |
| | 224 | 150 | 53 | 53 | 93 | 192 |
| | 235 | 150 | 53 | 87 | 68 | 208 |
| | 115 | 93 | 159 | 210 | 203 | 464 |
| | 147 | 87 | 141 | 205 | 192 | 495 |
| Mean | 181 | 116 | 107 | 187 | 114 | 262 |
| 30 Minutes | | | | | | |
| | 192 | 61 | 71 | 192 | 128 | 64 |
| | 171 | 55 | 82 | 208 | 117 | 52 |
| | 77 | 56 | 171 | 136 | 84 | 393 |
| | 70 | 65 | 179 | 118 | 95 | 364 |
| | 171 | 118 | 214 | 68 | 154 | 236 |
| | 171 | 112 | 237 | 86 | 138 | 196 |
| Mean | 142 | 78 | 159 | 135 | 119 | 218 |

Table C9. Effect of Laundering Temperature and Detergent on Terbufos in Laundering Solution (ng/150 ml)

| | Detergent | | No detergent | |
|---|---|---|---|---|
| | Low tem. | High tem. | Low tem. | High tem. |
| Nitrile | | | | |
| | 268 | 364 | nda | nda |
| | 374 | 370 | nda | nda |
| | 623 | 499 | nda | nda |
| | 623 | 375 | nda | nda |
| | nda | 703 | nda | nda |
| | nda | 596 | nda | nda |
| Mean | 315 | 485 | 0 | 0 |
| Neoprene | | | | |
| | 97 | 333 | 129 | 424 |
| | 146 | 286 | 129 | 480 |
| | 384 | 373 | 806 | 330 |
| | 549 | 314 | 784 | 290 |
| | 180 | 280 | 734 | 129 |
| | 235 | 347 | 560 | 162 |
| Mean | 265 | 322 | 524 | 303 |
| Barrier laminate | | | | |
| | 1014 | 1915 | 164 | 1732 |
| | 969 | 2296 | 108 | 1672 |
| | 3891 | 701 | 80 | nda |
| | 3181 | 784 | 93 | nda |
| | 549 | 4928 | 260 | 1960 |
| | 560 | 5611 | 240 | 2130 |
| Mean | 1694 | 2706 | 158 | 1249 |

tem. = temperature

Table C10. Effect of Laundering Temperature and Detergent on Tefluthrin in Laundering Solution (ng/150 ml)

| | Detergent | | No detergent | |
|---|---|---|---|---|
| | Low tem. | High tem. | Low tem. | High tem. |
| Nitrile | | | | |
| | 63 | 61 | 34 | 141 |
| | 75 | 55 | 21 | 135 |
| | 67 | 56 | 169 | 59 |
| | 71 | 65 | 163 | 76 |
| | 59 | 118 | 69 | 229 |
| | 56 | 112 | 65 | 176 |
| Mean | 65 | 78 | 87 | 136 |
| Neoprene | | | | |
| | 63 | 192 | 177 | 153 |
| | 67 | 208 | 179 | 165 |
| | 102 | 136 | 169 | 124 |
| | 117 | 118 | 166 | 124 |
| | 204 | 68 | 58 | 59 |
| | 148 | 86 | 69 | 59 |
| Mean | 117 | 135 | 136 | 114 |
| Barrier laminate | | | | |
| | 92 | 64 | 75 | 97 |
| | 100 | 52 | 72 | 112 |
| | 67 | 393 | 186 | 147 |
| | 67 | 364 | 189 | 106 |
| | 238 | 236 | 63 | 82 |
| | 258 | 196 | 67 | 82 |
| Mean | 137 | 218 | 109 | 104 |

tem. = temperature

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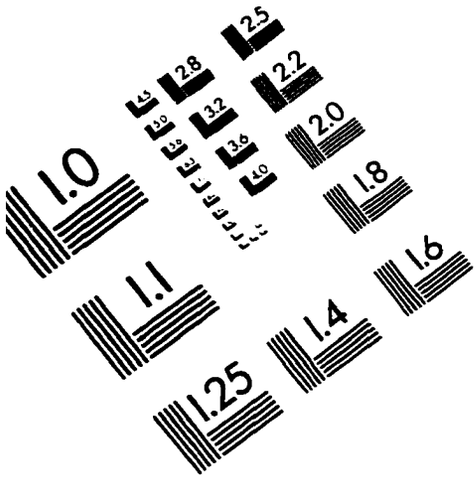


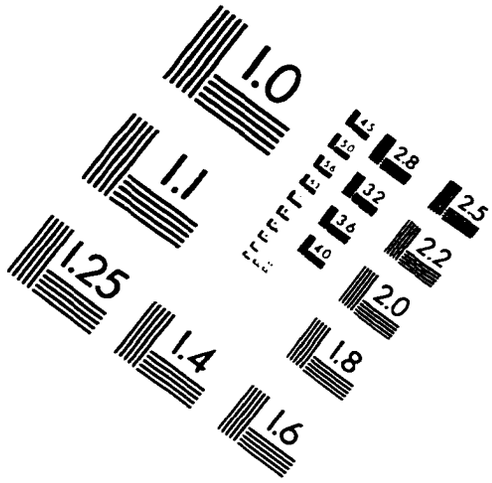


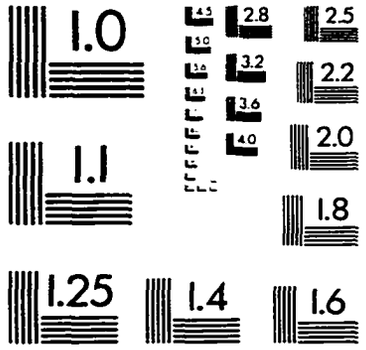


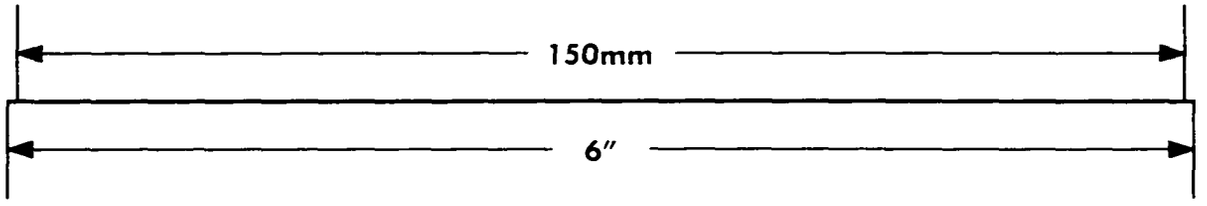


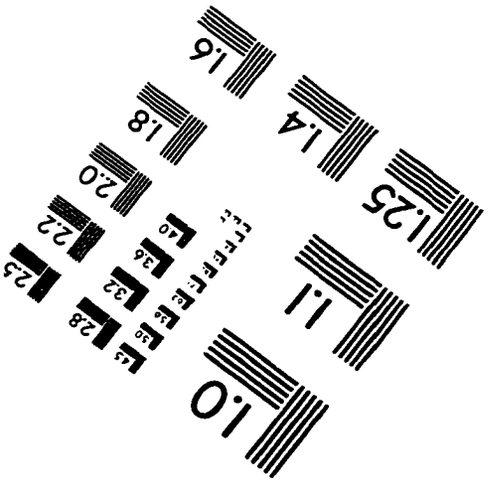


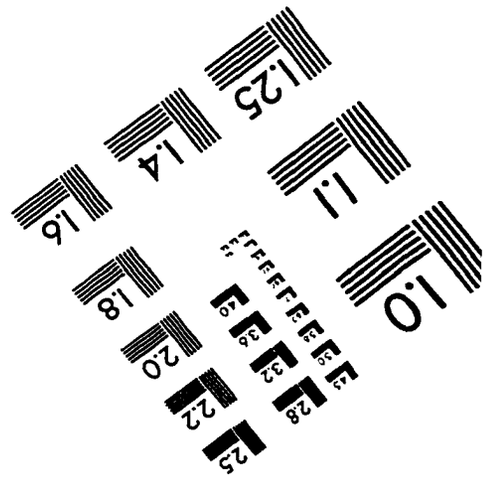


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